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Studies On The Recovery Of Useful Chemicals From Waste And Secondary Materials

A Thesis By

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CONTENTS

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DECLARATION

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S.C.Boddington.

ABSTRACT

Chapter 1 of the thesis introduces the technique of hydrometallurgy, and describes its background in relation to pyrometallurgy, the chemical methods used in hydrometallurgy and its application to metal recovery, with particular reference to the recovery of metals as useful compounds.

Chapters 2 and 3 show that hydrometallurgical methods can be applied to recovery of metals, as useful compounds, from waste and secondary materials. Chapter 2 descibes the recovery of nickel from a spent industrial catalyst as a smelting grade nickel oxide. Two different recovery concepts are investigated, the first involving the precipitation of the primary metal leaving impurities in solution, and the second involving the separation of impurities and leaving the primary metal in solution. Chapter 3 descibes an investigation into the recovery of zinc and copper, as commercially useful chlorides, from industrial waste, and it is shown, on a laboratory scale, that the recovery route can be integrated into an established manufacturing process with advantage.

Chapter 4, the final chapter, describes ion exchange and reviews the practical application of anion exchange resins to the hydrometallurgical recovery of metals. This is followed by a review of the exchange resin poly-4-vinyl pyridine, and a study into the practical application of the resin to the extraction of metals from solution. The metals chosen for investigation are a selection of those most often present as impurities in hydrometallurgical solutions. It is shown that the resin exhibits good metal selectivity under various experimental conditions.

CHAPTER 1

INTRODUCTION - HYDROMETALLURGY, AND THE WORK IN THE THESIS.

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1.1 Introduction

The traditional view of metal production, particularly of non-ferrous metals, is the treatment of primary ores by pyrometallurgical techniques. This can also be said about metal recovery from secondary ores and waste arisings. However, with the introduction of legislation in many industrial countries during the 1960's and 1970's, aimed at curbing enviromental pollution, the development of alternative methods to pyrometallurgy, became of importance. The alternative techniques investigated were those of hydrometallurgy, which can be described as the method of winning metal values by leaching of the raw material and subsequent chemical treatment of the arising. In this way, pyrometallurgical processing is avoided, therefore easing the difficulties associated with the compliance of anti-pollution laws. A comparison of hydrometallurgy and pyrometallurgy has been reviewed [1].

Although during the last 20 to 30 years, pyrometallurgical techniques and the reduction of fume output to the enviroment have improved, hydrometallurgical processing at the present time, does play an important role in metal recovery. However, this role has shifted from the "enviromentally friendly alternative", to one focussed on the processing of low grade ores and waste arisings, often involving chemically complex raw materials which would otherwise be economically unviable to process by pyrometallurgy. This shift in role has come about mainly because:

1) A gradual awareness of the finite nature of the Earths resources has occured resulting in more importance being placed on the use and recyling of lower grade ores and secondary materials, which are

often relatively complex chemically, and therefore cannot be processed by conventional pyrometallurgy.

2) Industry is more competitive, placing more emphasis on economics. A drawback of pyrometallurgy is the final stage of conversion to metal is often the most expensive.

It therefore follows that advantage can be gained if relatively inexpensive low grade ores and secondary arisings are used for recovery of the metal value and that, provided a commercial outlet is available, the metal value is recovered as a commercially useful metal compound involving simple hydrometallurgical techniques.

Examples of waste arisings are:

1) Spent catalysts - source of Ni.
2) Anode sludges - Platinum group metals, Se and Au.
3) Flue dusts - Zn, Sn and Cu.
4) Alloy scrap - Co and Mn.

1.2 Hydrometallurgy

The great strength of hydrometallurgy is the large number and variety of techniques that are available. Indeed, in principle, all the techniques of classical inorganic chemistry are at hand for hydrometallurgical processing plus relatively recent developments such as solvent extraction and ion-exchange resins.

Stages in the hydrometallurgical recovery of a metal value can be described as follows:

a) Characterisation of the sample by analysis - usually involving the determination of the elemental composition of the sample and the compounds present, by, for example, X-ray techniques.

b) Sample pretreatment - e.g. crushing.

c) Leach treatment - Most commonly by a suitable acid.

d) Treatment of the liquor to remove impurities - Usually by chemical means, e.g. controlled precipitation and ion exchange techniques.

e) Recovery of the principal metal value - As a commercially useful compound, by precipitation or crystallisation, or as a metal by electrolysis.

f) Purification of the product - e.g. washing

g) Final analysis of the product.

A schematic representation of the above is shown in figure 1.1.

Hydrometallurgy is concerned with metals in solution, and therefore the leach treatment to solubilise the metal value, is fundamental to the recovery technique. Leaching is usually performed

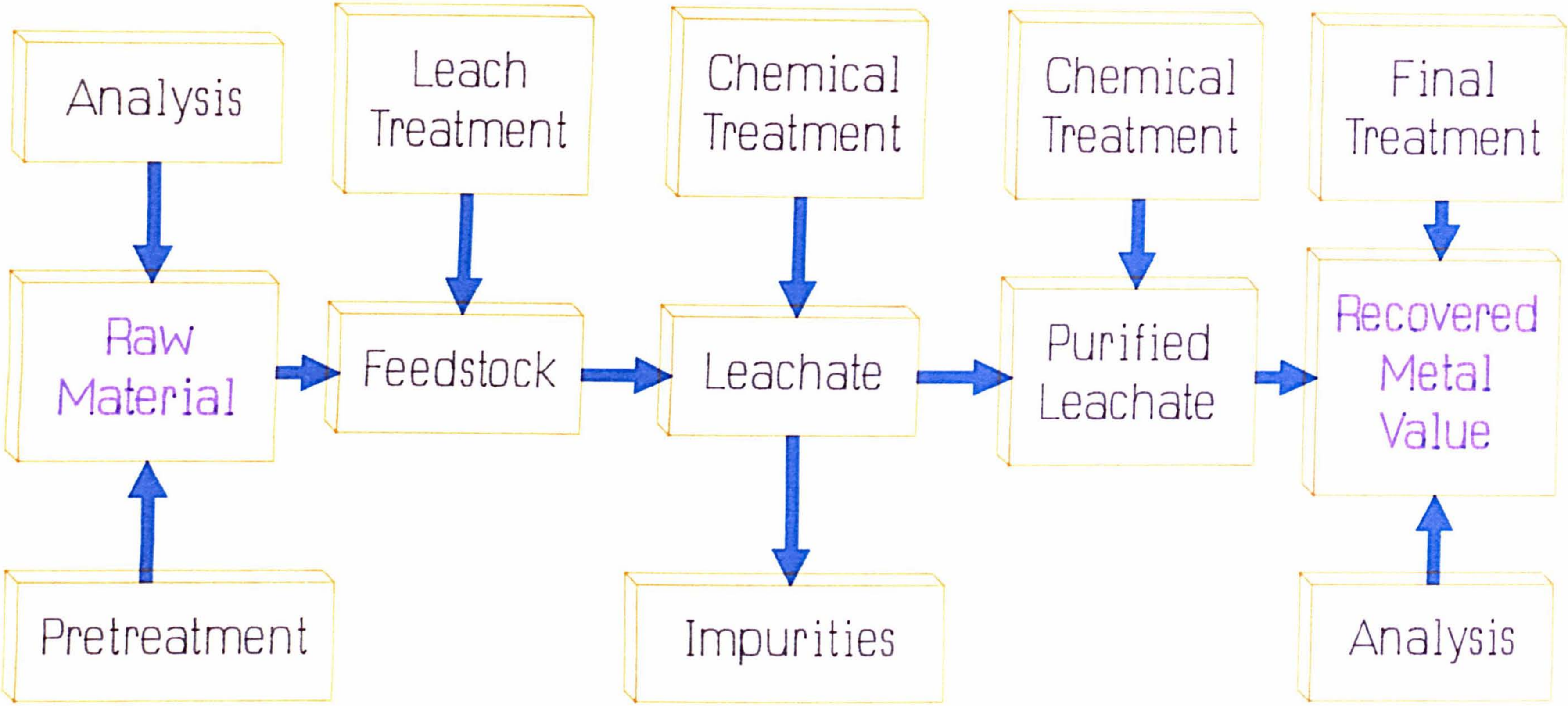

Figure 1.1 Typical Scheme For The Hydrometallurgical Recovery Of A Metal Value.

with a suitable acid, under oxidising conditions, and most often with hydrochloric acid in combination with other chloride based reagents, such as $CuCl_2$, $FeCl_3$ or NaCl, and with chlorine or air [2]. However, sulphuric acid and nitrate based leach treatments are also used [3,4,5]. The use of higher temperatures and pressures during the leach stage is advantageous, particularly in increasing the leach rate, and in allowing the use, to greater effect, of gaseous and volatile reagents, such as oxygen and ammonia.

Two main parameters can be cited as critical in determining the behaviour of metal species in solution, these are solution pH and oxidation potential. These are therefore the major variables available, for use by the hydrometallurgist, when considering the methods of separation of the impurities from the primary metal in the leachate, (the filtered liquor arising from the leach treatment). The pH of the metal containing liquor determines the solubility of hydrolysed metal species and the oxidation potential controls the valency of the metal species which often directly governs the solubility.

The hydrolysis of metal ions, (and subsequent precipitation), can be represented by an equilibrium of the type,

$$M^{n+} + nH_2O \rightleftharpoons M(OH)_n + nH^+$$

and it is generally true that tri- and tetravalent metal ions hydrolyse under more acidic conditions than mono- and divalent ions. Figure 1.2 shows the pH at which the precipitation of hydroxides, for various metal ions, occurs, and shows, for example, that the separation of Fe^{3+} and Ni^{2+}, and of Al^{3+} and Zn^{2+} can be effected simply by pH adjustment. In fact one of the most important, and widely used separations of this

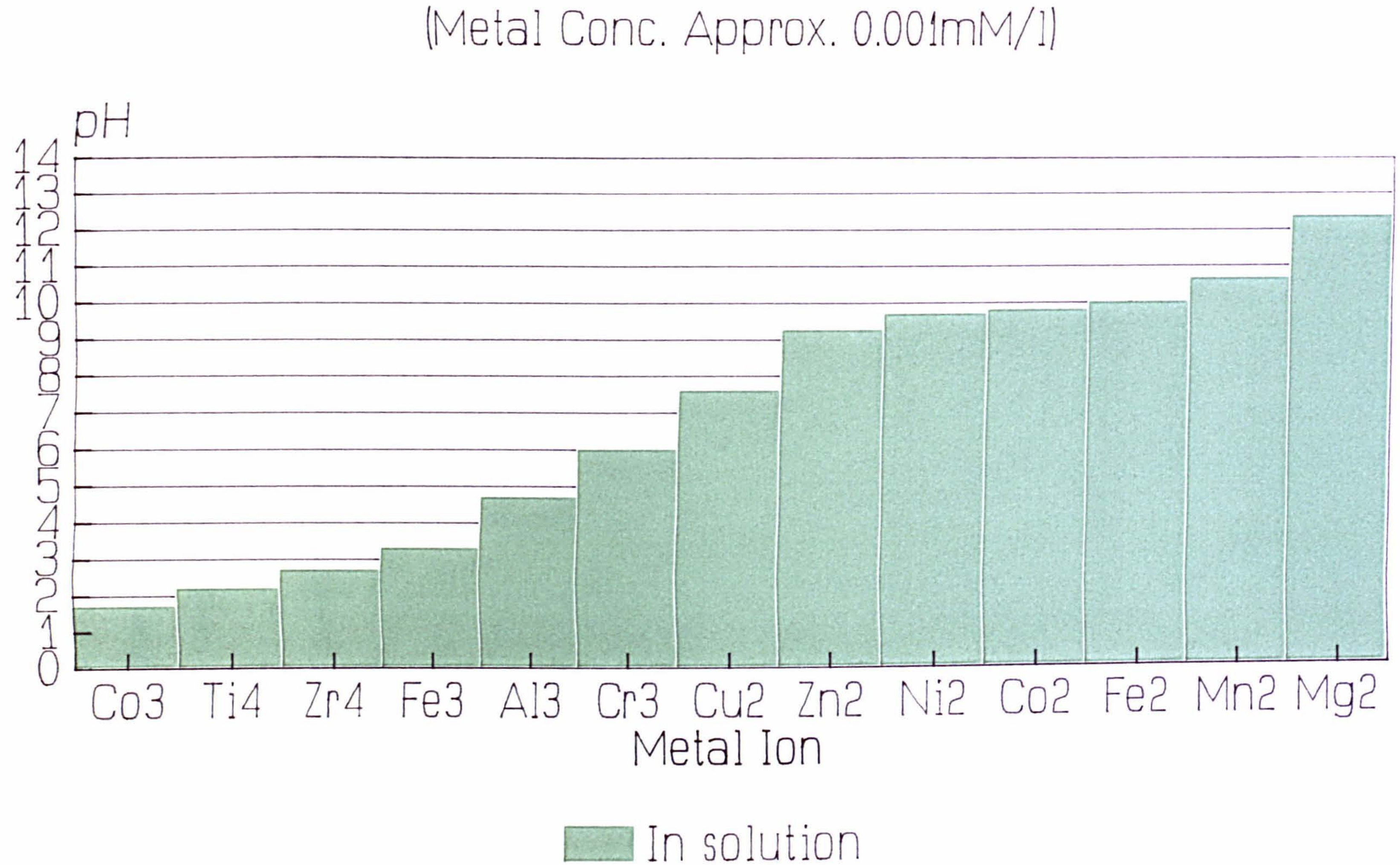

Figure 1.2
Precipitation Of Hydroxides

Reference [6]

kind, involves the precipitation of a Fe^{3+} impurity from solutions of other metal ions, as hydroxide or a hydroxy sulphate, [7,8,9].

Further precipitation techniques which are available to the hydrometallurgist for the separation of metals can be cited, these include,

1) Precipitation of sulphides with variation in sulphide concentration and pH.

2) Crystallisation of ammonium metal sulphates with varying temperature and sulphate concentration, [10].

3) Precipitation of insoluble metal compounds with various specific ligands, for example in the separation of palladium from rhodium trichloride solutions as a Pd-DMG complex, [11].

Although the major anion in solution does not generally affect the precipitation techniques described above, (apart from the ammonium metal sulphate precipitation), chloride solutions are now more frequently used than in the past. This increased attention toward chloride based hydrometallurgy can be attributed to various factors:

a) Construction of equipment resistant to the highly corrosive nature of chloride solutions, as opposed to sulphate solutions, is now less of a problem.

b) The formation of metal-chloro complexes in solution allows the use of techniques for separation which would not be possible in sulphate solutions.

c) Chloride can often be recovered as hydrochloric acid, via HCl fume, enabling a route for recyling.

d) Many metal chlorides are very soluble compared to the corresponding sulphates, which allows the use of more concentrated process solutions, and therefore reduces the volumes of liquor needed to be handled.

Factor b) above, is of great importance when considering the versatility of hydrometallurgy, because the formation of anionic metal-chloro complexes is fundamental to the significant use of anion exchange techniques. The formation of these complexes and their use in metal recovery involving anion exchange resins, is dealt with in detail in chapter 4 of this thesis.

Ion exchange techniques in general can be divided into two main divisions, namely liquid-liquid and liquid-solid exchange, involving solvent extraction and ion exchange resins respectively. Sub-divisions can also be described, which are applicable to both. These are cation and anion exchange, general examples of which are given below:

Cation exchange - $M^{n+}{}_{aq} + nRH_{org} \rightleftharpoons R_nM_{org} + nH^{+}{}_{aq}$

Anion exchange - $MCl_6{}^{n-} + nRCl_{org} \rightleftharpoons R_nMCl_{6org} + nCl^{-}{}_{aq}$

R represents the exchange active ligand in the organic species, which is often alkyl phophate groups in cation exchange and alkyl amines in anion exchange. Chelation exchange is also possible, and involves the direct coordination of a metal atom to an atom, often an amine nitrogen, in the organic ligand.

Of the two techniques, solvent extraction has probably the most widespread application in industrial hydrometallurgy, examples of which include the nickel refining Falconbridge Matte Leach Process [12], and the recovery of zinc from pyrites cinders in the Zincex Process [13].

Following the application of purification techniques to the leachate, is the final stage in the hydrometallurgical recovery of metal value, of winning the value in a commercially useful form, either as a metal, usually by electrolysis, or as a compound.

Electrolysis can be defined as the chemical decomposition of an electrolyte, in a dissolved or molten state, by the passage of an electric current, via suitable electrodes. In the context of hydrometallurgy, the result of the decomposition is the deposition of the metal of value at the cathode.

The electrowinning of metal values is an established part of hydrometallurgy, especially for the worlds non-ferrous metals production and in particular zinc, (e.g. Sherrit Gordon/Cominco process [3]), and copper, (e.g. Duval's CLEAR process [2]). However, in recent years the electrowinning stage in hydrometallurgy has been investigated critically [14,15,16], and several conclusions have been drawn [17], the major one being that hydrometallurgical recovery in combination with an electrowinning stage often results in an energy input comparable to pyrometallurgical recovery. In this light, the avoidance of the electrolysis step, by the recovery of the metal value as a commercially useful compound, could, in many cases, be economically advantageous. With this concept, there are a number of points to consider:

a) The commercial outlet(s) for the metal compound, and their specifications for the product, must be identified.

b) The size of the market will determine the competitiveness for the product, and therefore will reflect its market value.

c) What tolerance on the purity of the primary recovered product is allowed? This is a very important consideration because in some cases, the impurities present in the crude precipitated or crystallised product, will be tolerated by a specific market outlet, so avoiding further purification, and therefore, expense.

d) It may be advantageous to convert the primary product to a more specialised compound, which although may have a smaller market, will, by its speciallity, command a higher value.

1.3 About the thesis.

The remainder of this thesis comprises three chapters of practical work, followed by three appendices.

Chapters 2 and 3 put into practice, on a laboratory scale, various aspects of hydrometallurgy, and are concerned with, respectively:

a) The development of a process for the recovery of the metal value from a waste arising, as a commercially useful compound.

b) The modification of an established industrial process to allow greater flexibility in the choice of feedstock.

Chapter 4 describes an investigation into the use of a relatively new exchange resin to the separation of metals from solution, and also gives details on various general aspects of anion exchange, particularly when applied to metal recovery.

The appendices are concerned with the three major analytical techniques used in the practical work throughout the thesis, and describe the techniques, their practical application in the work and include information, and data, on aspects relating to their practical application.

Wherever possible in the practical work, emphasis was placed on using simple techniques, involving common and relatively inexpensive reagents, because although the work was done on a laboratory scale, the possibility of its application to industry, was always an important and major consideration.

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CHAPTER 2

THE RECOVERY OF THE NICKEL VALUE, AS A NICKEL OXIDE SUITABLE FOR SMELTING, FROM A SPENT LOW GRADE NICKEL CATALYST.

List of Tables and Figures.

2.1 Introduction.

A the present time, some use is being made of spent, high nickel content catalysts for the recovery of their nickel value. However, spent catalysts, low in nickel (less than 15 to 20%), are little used for nickel recovery because of the problems, both chemical and economic, which are associated with metal recovery from lower grade catalysts. The annual arising in the U.K. of spent catalysts low in nickel is approximately 500 tonnes, and therefore, considerably more nickel recovery and recycling could be achieved if suitable processes for treating these arisings was developed.

The work described in this chapter, deals with the development of two processes for nickel recovery from a spent catalyst containing approximately 17% nickel.

Method 1

A spent catalyst leachate is chloridised with hydrogen chloride gas, to precipitate nickel from solution as nickel chloride. An initial increase in the Ni:secondary metal ratio, a measure of the purity of the compound, is achieved in this way. A further increase is achieved by washing, or otherwise, of the precipitate.

Method 2

Various techniques are used to remove secondary metals from a spent catalyst leachate, to produce a concentrated, purified nickel chloride solution.

In both methods, the purified nickel concentrates are then treated to give a nickel oxide of a purity suitable for the smelting industry.

The methods described are totally different in concept, (figure 2.1), and provide a means of comparing different aspects of the chemistry of nickel recovery.

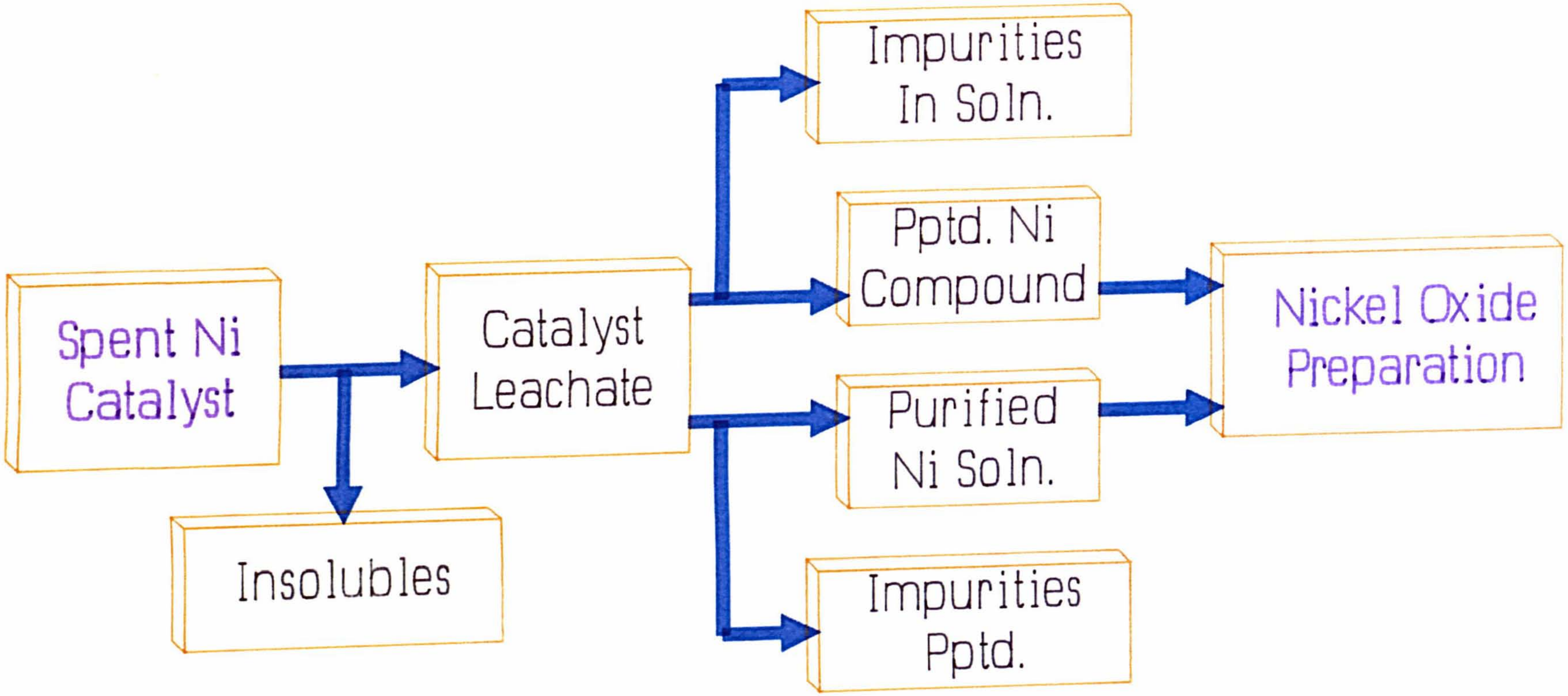

Figure 2.1 Two Approaches To Nickel Recovery.

2.2 Catalyst Analysis.

A sample of spent nickel catalyst was received from Ireland Alloys Ltd.

It was immediately apparent that the material was of a very heterogeneous nature, comprising of lumps of various sizes, (1 to 5cm), seemingly of different composition, together with finer granules and powder. An analysis received is given in table 2.1.

Table 2.1 Catalyst Analysis.

Content	% Wt.	Content	% Wt.
Ni	17.7	S	0.75
Co	0.15	Fe	30.0
Cu	9.5	Water	27.5
Mn	0.1	Non-metals	3.2
C	7.9		

A sample of catalyst was crushed and sieved through a 2400 micron, 7 mesh seive. Because of the heterogeneity of the presieved material, sufficient catalyst was crushed, sieved and homogenised as far as possible, to last the complete series of experiments described in this chapter. A fair degree of confidence could therefore be placed on the consistency in composition of each sample, taken from the sieved stock, for use in subsequent experimental work.

Analysis for total Ni content of the sieved catalyst using XRF and a standard addition method, gave a figure of 16.4%.

A semi-quantitative analysis of the elemental composition of the sieved catalyst, using an SEM with EDAX attatchment, (Appendix 2), showed a considerable proportion of Ca and Zn to be present (5 to 10%), in conflict with the works analysis received.

Table 2.2 shows the apparent metal composition of the sieved catalyst derived from the supplied analysis and the EDAX results. Also given, is the specification for the smelting grade nickel oxide, as supplied by Ireland Alloys Ltd. The specification shows the importance to the smelting industry, of providing a nickel oxide low in base metal concentrations. Lighter metals, such as Zn and Ca, which slag out during smelting, are less troublesome.

<u>Table 2.2 Catalyst And Nickel Oxide Analyses.</u>

Content	Catalyst (approx %)	NiO spec.* (%)	Content	Catalyst (approx %)	NiO spec.* (%)
Ni	17	>50	Cd	--	0.2
Co + Cu	10	3	Mo	--	0.5
Fe	30	No spec.	Pb	--	0.1
Mn	0.1	No spec.	Non-mets	3.2	S 0.2, P 0.2
Sn	--	0.1	C	7.9	No spec.
Ca	5-10	No spec.			
Zn	5-10	No spec.			

(*Max. unless stated).

2.3 Solubilisation of the nickel content of the catalyst.

The use of a sulphuric acid leach was ruled out, primarily to avoid sulphur contamination of the product nickel oxide, (a 0.2% limit on the sulphur content is imposed on the oxide specification).

Hydrochloric acid was chosen as a suitable leaching agent for the catalyst because advantage could be taken, if necessary, of HCl recycling within the recovery process, and chloride solutions have a greater scope for the application of recovery techniques. (See section 1.2).

To study the efficiency of a hydrochloric acid leach on the Ni content of the catalyst, approximately 50g samples of sieved catalyst were treated with 80ml volumes of acid of various strengths. A wt. of catalyst:leach solution ratio of 0.625g/l was found to be a good value, giving a well concentrated leachate, without the leach mixture being too viscous.

One hour, with vigorous stirring was allowed before filtration of the leach mixture. Total Ni content of the combined leach filtrate/residue washings, (the leach residue was washed with either 2 x 50ml water, 20%, 80% or conc. HCl), was determined by A.A.S. Results are given in table 2.3.

In the case of the 20% acid treatment, the strength of the acid was chosen to be just sufficient to react stoichiometrically with the catalyst, giving a leachate with a pH of about 2.

If temperatures above ambient were used for leaching, the experiments were conducted under reflux.

Table 2.3 Leach Results.

Leach	Temp. (°C)	Wt.cat. (g)	Wt.res. (g)	Ni (g) extract.	%Ni (Relative to cat.)	%Residue (Relative to cat.)
Water	70	51.8	28.0	3.05	5.9	54.0
20%HCl	21	49.5	13.5	6.01	12.1	27.2
20%	21	50.3	12.4	6.20	12.3	24.6
20%	80	50.3	15.7	6.14	12.2	31.2
20%	80	50.5	15.7	6.07	12.0	31.1
80%	21	49.5	12.7	6.28	12.7	25.7
80%	21	49.5	13.7	6.40	12.9	27.7
80%	80	49.8	10.0	6.43	12.9	20.1
80%	80	50.3	10.7	6.53	13.0	21.3
Conc.	21	49.9	11.7	6.28	12.6	23.4
Conc.	21	49.8	11.6	6.30	12.6	23.3

The results show that besides a hydrochloric acid leachable nickel content of the catalyst, there remained a proportion of the nickel content which was resistant to a simple acid leach, equivalent to about 25% of the total Ni content. In an attempt to dissolve this remaining nickel, the use of a strongly oxidising leach was investigated. Experiments using 20% and 80% acid at 21°C were repeated, but during the leach period, chlorine gas was passed through the leach mixture at a rate sufficient to continually saturate the leach mixture with dissolved chlorine. Results of this experiment are given in table 2.4.

Table 2.4 Oxidising Leach Results.

Leach	Temp. (°C)	Wt.cat. (g)	Wt.res. (g)	Ni (g) extract.	%Ni	%Residue
					(Relative to cat.)	
20%HCl	21	49.4	15.4	6.07	12.3	31.2
20%	21	50.0	14.1	6.10	12.2	28.2
80%	21	49.9	12.6	6.30	12.6	25.2
80%	21	50.1	12.8	6.28	12.5	25.5

As can be seen from table 2.4, no improvement in Ni extraction was achieved.

In view of these results, it was decided that further work aimed at improving leaching efficiency, would not be worthwhile at this stage. Improvements, if achieved, would almost certainly lead to a recovery process no longer dealing with essentially simple chloride solutions, and would therefore necessitate the involvement of more complex recovery routes. Semi-quantitative analyses of the leach residue, involving EDAX, showed them to be mainly composed of Si, S and Ca, with smaller quantities of Cu, Fe, Al and Ni. Considerable elemental carbon also seemed to be present.

With a hydrochloric acid leach, approximately 73 to 79% of the total Ni content of the catalyst can be extracted. The remaining Ni seemed to be very resistant to leaching with hydrochloric acid, even under strongly oxidising conditions.

The effect of temperature on extraction efficiency is negligible - no advantage is gained by external heating of the reaction. (The leach reaction was found to be slightly exothermic, raising the temperature of the solution from 21°C to approximately 30°C.).

The effect of acid strength, on extraction, was also found to be negligible.

The effect of leach conditions, on overall solubilisation of the catalyst, does show some variation. In the case of a strongly acid leach, especially at high temperature, considerably more solubilisation occurs, compared to a leach with 20% HCl at high temperature - approximately 10% more, almost all of which is unwanted solubilisation.

2.4 Method 1 The Precipitation Of Nickel Chloride From The Catalyst Leachate With Hydrogen Chloride Gas.

2.4.1 Introduction.

In concentrated hydrochloric acid, the majority of metals can exist as soluble anionic chloride complexes. Indeed, extensive use is made of this fact for the retention of metal species, from hydrochloric acid, on anion exchange columns. [1,2,3,4,15]. Separation of one metal from another is achieved by utilising the variations in stability of each metal complex, with varying acid concentration. Examples of well known anionic chloro-complexes include $FeCl_6^{3-}$, $CuCl_4^{2-}$ and $ZnCl_4^{2-}$. Although most metals are able to form these complexes in hydrochloric acid, there are exceptions. Ni^{2+}, Al^{3+}, the Alkali and Alkaline Earth metals are examples.

With knowledge of the facts mentioned above, it was apparent that the possibility may exist for the development of a technique, for the separation of nickel from other metals in the catalyst leachate, involving HCl gas. In a concentrated hydrogen chloride solution, the inability of Ni^{2+} to form complexes, would significantly reduce the solubility of nickel chloride, relative to other metal chlorides. A subsequent literature survey revealed a few references to earlier work on the use of HCl gas and concentrated hydrochloric acid to reduce the solubility of $NiCl_2$ [16,17]. Seidel and Fischer [5], investigated the solubility of NaCl, KCl, NH_4Cl, $BeCl_2$, $AlCl_3$ and two double chlorides in hydrochloric acid of various concentrations, at 0°C. The variation in the solubility of the salts were then used as a basis for separations.

Kubo and Toniguchi [18], described a method for the separation of Ni^{2+} and Co^{2+}, whereby a chloride solution was saturated with HCl gas to precipitate the nickel content, leaving a cobalt chloride solution of acceptable commercial purity. The use of HCl saturated organic solvent-water mixtures has also been investigated for metals separation [6,7].

Preliminary work on the solubility of nickel, as nickel chloride, in HCl saturated solutions at 21°C, yielded promising results. With a pure $NiCl_2$ solution, nickel solubility was reduced from approximately 160g/l Ni in water, to less than 10g/l, by saturating the solution with HCl gas. Precipitates obtained in this way, seemed anhydrous in nature, changing colour from yellow when in contact with the HCl solution, to green on exposure to air. Previous work , by other workers, suggests that the precipitated compound is $NiCl_2.2H_2O$ [18,19]. A further reduction in the solubility was achieved by saturating the solution with the gas at 0°C. However, it was decided that subsequent detailed experiments involving catalyst leachates, would be conducted at room temperature. This would avoid the practical problems associated with operating systems at temperatures well below ambient, a fact particularly important in industry, where economic constraints would also be involved.

Hydrogen chloride is a relatively expensive gas, compared to other widely available gases, so efforts to recycle the gas within the recovery process were considered important.

A preliminary scheme for the separation of nickel from the catalyst was devised and is illustrated in figure 2.2.

Hydrogen chloride gas, used for the precipitation of nickel chloride from the catalyst leachate, would be recycled in the form of a concentrated solution, and would be used csubsequently as a leach solution for a fresh batch of catalyst. The loss of nickel within the process, due to incomplete precipitation, would therefore be prevented.

As a simplified description, the method proposed is based on a series of leach-precipitation cycles, where the only input to the system would be fresh catalyst and HCl gas, and the only outputs would be leach residue (acid insolubles), and the precipitated nickel chloride.

Sections 2.4.2 and 2.4.3 describe an investigation into the recovery scheme proposed in figure 2.2. In the experimental work, particular attention is given to the effect on the precipitation and purity of the nickel chloride, of continually recycling of the solution involved.

The purification of the chloride by washing and anion exchange, and the subsequent preparation of nickel oxide, are then described.

In the remainder of section 2.4., conclusions drawn from the results obtained, are discussed, and an overall summary of the method is presented.

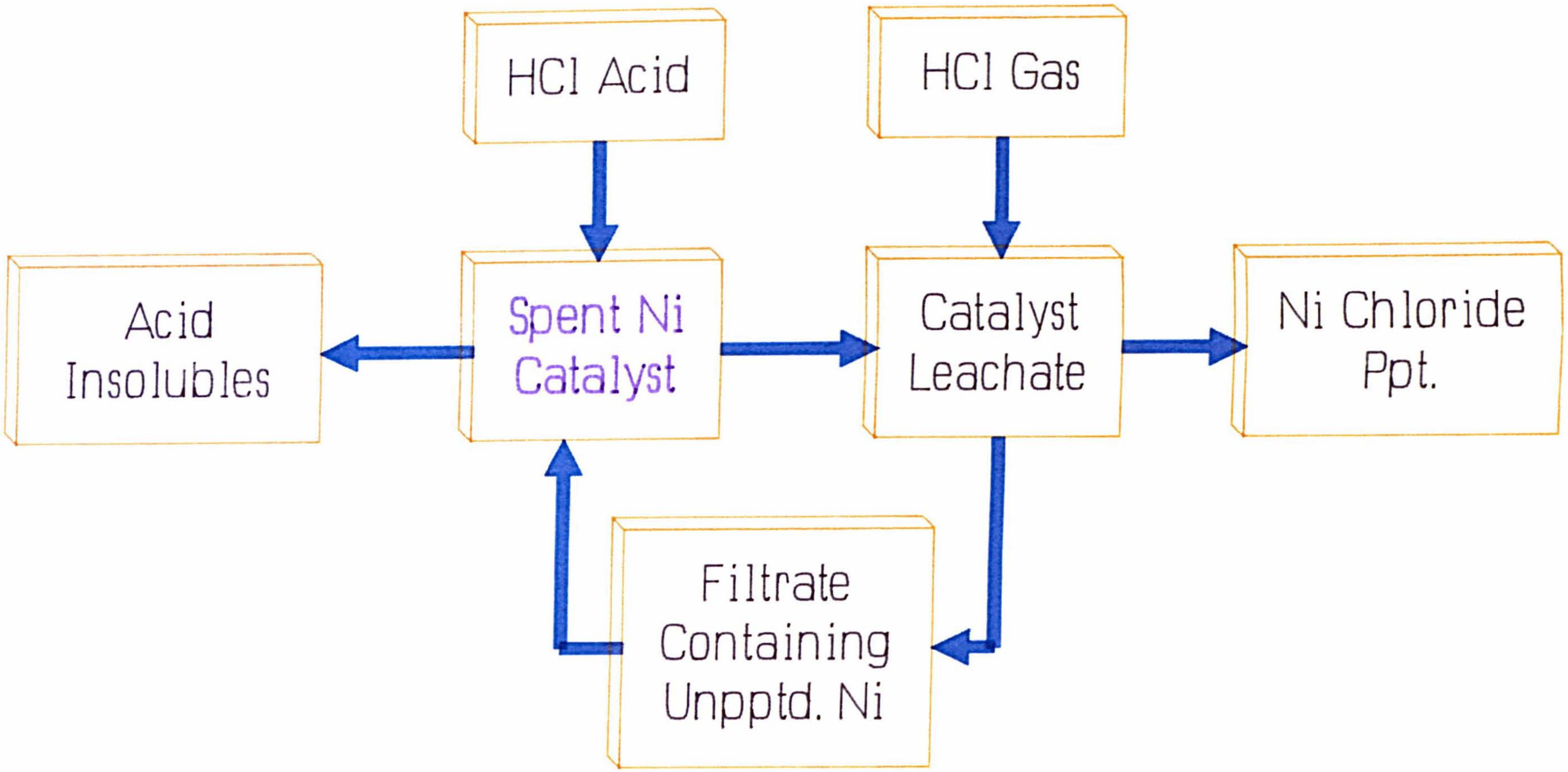

Figure 2.2 Proposed Scheme For Ni Recovery

2.4.2 Nickel chloride precipitation.

Preliminary work on nickel chloride precipitation by absorbing dry HCl gas into catalyst leachates, (obtained by leaching 50g samples of catalyst with 80ml volumes of concentrated hydrochloric acid), indicated that prolonged absorption of dry HCl gas, leading to complete saturation of the leachates, was not necessary in order to achieve a considerable reduction in nickel chloride solubility. Table 2.5 shows the results obtained by following the precipitation in terms of %w/w HCl content of the reaction medium, the specific gravity of the liquor and the nickel chloride solubility within the liquor.

Table 2.5 HCl Absorption And Nickel Chloride Solubility.

%HCl (w/w)	S.G.	$NiCl_2$ solubility (g/l Ni)	Remarks
28.9	1.419	up to 160	No pptn.
31.7	1.380	14.7	Initial bulk pptn.
33.8	1.366	6.7	Further pptn.
36.7	1.355	2.2	Further pptn.
38.2	1.355	1.3	HCl satd. liquor

In view of these results, it was decided for subsequent experimental work, HCl absorption would be ceased directly after the initial bulk precipitation. This would save on the quantity of HCl gas used and would avoid handling strongly fuming HCl solutions.

It was found that the filterability of precipitates obtained in this way was excellent. The handleability of the filter cakes was also found to be excellent, the cakes being compact and dry.

The solubility of $FeCl_3$, $ZnCl_2$, $CoCl_2$ and $CuCl_2$ in concentrated HCl solutions was investigated and found to be high, in most cases >100g metal per litre. Of the other metal chlorides found in the catalyst leachates, only $FeCl_2$ and $AlCl_3$ showed low solubility, 11g/l Fe and <5g/l Al respectively. Contamination of the precipitated $NiCl_2$ from $FeCl_2$ and $AlCl_3$ is unlikely to be significant because of the low concentrations of these compounds present in the catalyst leachates. (See 2.4.3).

2.4.3 Investigation into repeated leach/precipitation cycles.

Approximately 125g of sieved catalyst was added to 200ml of concentrated hydrochloric acid. The mixture was stirred for one hour with no external heating, and then filtered with a Buchner apparatus. Dry HCl gas was passed into the leach filtrate until the initial bulk precipitation had occured. The precipitate was filtered on a No.3 glass sinter, and maximum compression of the cake. Concentrated hydrochloric acid was added to the filtrate to return the volume to 200ml and the filtrate then used as a leach solution for a fresh 125g batch of catalyst. This leach/precipitation cycle was repeated a further 3 times. The filter cakes were analysed for metal concentration by A.A.S. and HCl content by titration with standard alkali and methyl red indicator. Experimental data and results are given in tables 2.6 to 2.9.

Table 2.6 Experimental Data For Leach Cycles.

Cycle	Wt.Catalyst (g)	Vol.Filtrate (ml)	Wt.Cake (g)	Vol.Filtrate After pptn(ml)
1	125.2	202	63.8	166
2	125.4	197	75.2	167
3	125.1	191	80.8	157
4	124.9	195	79.1	162

Table 2.7 Filter Cake Analyses.

Cycle	Wt. Metal in Cake (g) (% Metal in Cake)						HCl in Cake (%)
	Ni	Fe	Zn	Cu	Co	Al	
1	10.29	0.59	0.21	0.14	0.04	0.03	10.3
	(16.12)	(0.92)	(0.33)	(0.22)	(0.06)	(0.05)	
2	12.79	0.95	0.32	0.33	0.09	0.05	10.8
	(17.01)	(1.28)	(0.42)	(0.44)	(0.12)	(0.07)	
3	12.29	1.31	0.61	0.37	0.09	0.07	11.1
	(15.21)	(1.62)	(0.75)	(0.46)	(0.11)	(0.09)	
4	12.52	1.35	0.70	0.38	0.08	0.06	11.1
	(15.83)	(1.71)	(0.88)	(0.48)	(0.10)	(0.08)	

Table 2.8 Nickel Recovery By Precipitation.

Cycle	Wt.Ni in Leachate(g)	Ni Solubility in HCl satd Liq.(g/l)	% Ni pptd.
1	12.81	15.2	80.3
2	14.39	9.6	88.9
3	13.59	8.3	90.4
4	13.83	8.1	90.5

Table 2.9 Ni:Secondary Metal Ratio In Filter Cake.

Cycle	Fe	Zn	Cu	Co	Al
Original Cat.	2.6	4.6	11.7	86.3	59.9
1	17.4	49.0	73.5	257.2	343.0
2	13.3	40.0	38.8	142.1	256.0
3	9.4	20.1	33.2	136.5	176.0
4	9.3	17.9	32.9	156.5	209.0

The results show that following the first precipitation cycle, reasonable consistency was subsequently observed for volume reductions, %Ni precipitated, residual $NiCl_2$ solubility and the filter cake weight. No detrimental effect on the overall extraction of nickel from the catalyst, by repeated cycling of leach solutions, was apparent.

The purity of the precipitated nickel chloride decreased as the number of cycles increased. This was expected, because concentrations of secondary metals in solution would gradually increase through successive leach cycles.

2.4.4 Purification of precipitated nickel chloride by washing.

The effect of washing precipitated nickel chloride with concentrated hydrochloric acid, on the Ni:secondary metal ratios, was investigated.

Approximately 67g of filter cake, with a composition and initial Ni:secondary metal ratio typical of a third of fourth cycle precipitate, was slurried with 25ml of concentrated hydrochloric acid, (sg 1.18), and then filtered on a No.3 glass sinter. The filter residue was compressed as much as possible, to give a dry, compact cake.

The washing procedure was repeated a further 3 times using fresh 25ml volumes of acid to ultimately give a filter cake which had been washed 4 times.

Analyses of the filter cakes after each wash, for metal content by A.A.S., revealed the results given in table 2.10. Data on the solubilisation of nickel during each wash is given in table 2.11.

Table 2.10 shows that washing the filter cake with concentrated hydrochloric acid progressively increased the Ni:secondary ratios and hence the overall purity of the nickel chloride. Approximately a ten fold increase in ratios was achieved after two washes, with up to a fifty fold increase after 4 washes. The exception was the Ni:Co ratio - little increase was observed.

As expected, quantities of nickel chloride were solubilised by the

Table 2.10 The Effect Of Washing The Filter Cake On Metal Content.

Wash	% In Filter Cake (Ni:Secondary Metal Ratio)					
	Ni	Fe	Zn	Cu	Co	Al
Before wash	15.21	1.62	0.75	0.46	0.11	0.09
		(9.4)	(20.1)	(33.2)	(136.5)	(175)
1	17.04	0.79	0.30	0.23	0.11	0.04
		(21.7)	(57.4)	(75.1)	(152.4)	(410)
2	17.30	0.29	0.10	0.11	0.11	0.02
		(59.0)	(167.2)	(156.8)	(152.0)	(1003)
3	17.48	0.12	0.05	0.07	0.11	<0.01
		(145.7)	(327.8)	(249.8)	(154.3)	(>1700)
4	17.52	0.05	0.02	0.05	0.11	<0.01
		(320.9)	(1027)	(320.9)	(160.4)	(>1700)

Table 2.11 Effect Of Washing The Filter Cake On Nickel Content.

Wash	Wt.Ni Solub.(g)	%Ni Solub.	%Ni in Cake	% Overall Ni Solub.	Wt. Cake Solub.(g)	% Overall Cake Solubn.
Before	--	--	15.21	--	--	--
1	0.27	2.6	17.04	2.6	13.1	13.1
2	0.28	3.0	17.30	5.4	4.5	16.8
3	0.37	4.3	17.48	9.0	5.3	20.7
4	0.49	6.4	17.52	13.8	6.5	25.0

washing procedure. An increase of 2 to 3% on the overall Ni solubilisation occured after each wash.

2.4.5 Purification of precipitated nickel chloride by anion exchange.

As already pointed out in section 2.4.1, Ni^{2+} is an unusual metal ion because of its inability to form complex chloride anions in chloride solutions of any HCl concentration. This fact makes $NiCl_2$ solutions, containing other Transition Metal impurities, ideally suited to purification by anion exchange, because the majority of Transition Metal ions readily form complex chloride anions.

eg. $FeCl_3 + 3Cl^- \rightleftharpoons FeCl_6^{3-}$

$$FeCl_6^{3-} + 3RCl \rightleftharpoons R_3FeCl_6 + 3Cl^-$$

$$Cl^- + NiCl_2 + RCl \longrightarrow \text{No reaction.}$$

Where R = functional group of the exchange resin matrix.

Valuable work by Kraus and Nelson [4], showed that in hydrochloric acid Fe^{3+} can be retained by a strong base quarternary ammonium anion exchange resin, if the HCl concentration is greater than about 1M/l; Cu^{2+} in HCl >3M/l; Co^{2+} >7M/l, whereas Zn^{2+} can be retained in solutions of any HCl concentration.

In the present work it was thought possible that a nickel chloride solution, prepared by dissolving filter cake in water, could be purified by simply passing the solution through an anion exchange column. Because of the high concentration of chloride ions originating from $NiCl_2$, the addition of hydrochloric acid would be unnecessary. This could allow a simple route for the recycling of the HCl content of the filter cakes by evaporation, (and subsequent recovery), before dissolution of the cakes in water. Figure 2.3 shows the scheme.

The proposed method for the purification of the nickel chloride was investigated.

15g samples of unwashed filter cake were heated at 105°C for 2.5 hours to evaporate HCl, before dissolution of each sample in 20ml water, to give solutions containing approximately 125-135g/l Ni (2.15 to 2.35M/l Ni; 4.3 to 4.7M/l Cl^-) at pH 1.5. (Maximum nickel solubility as $NiCl_2$ is about 160g/l). Loss of weight on heating was found to be 41 to 47%. The solutions were then percolated through an anion exchange column, packed with Amberlite IRA-400, a strong base, quarternary ammonium, anion exchange resin in the chloride form. The treated solutions were then analysed for metal content by A.A.S.

Further solutions were prepared, treated and analysed in a similar way, without the prior heat treatment of the filter cakes. Solutions prepared in this way, had similar nickel concentrations to those prepared from heat treated filter cakes, but also contained a hydrochloric acid concentration of 2.0 to 2.2M/l, giving a total chloride concentration of 6.3 to 6.9M/l.

Results of these experiments are given in table 2.12.

Table 2.12 shows that very good reductions in concentrations of Fe, Zn and Cu were achieved by anion exchange, even at pH 1.5. Under

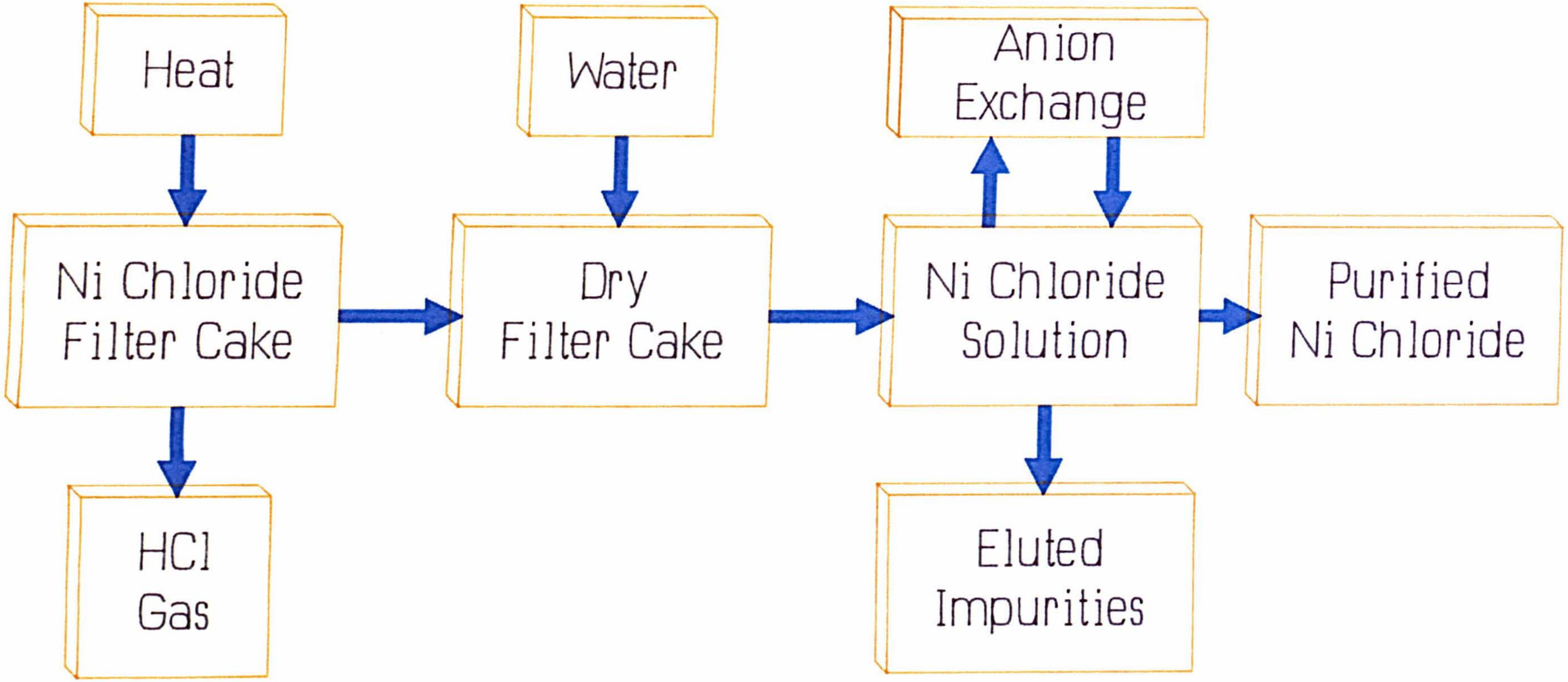

Figure 2.3 Nickel Chloride Purification

Table 2.12 Solution Treatment By Anion Exchange.

	Ni:Secondary Metal Ratio				
	Fe	Zn	Cu	Co	Al
Before Treatment	12.5	20.0	39.1	174.7	187.3
After Treatment					
(pH 1.5)					
Solution 1	5734	50,000	8148	179.0	187.8
Solution 2	5207	50,000	8270	180.7	187.7
(2.0-2.2M/1 HCl)					
Solution 3	>50,000	>50,000	>50,000	640.0	189.1
Solution 4	>50,000	>50,000	>50,000	575.6	187.4

the experimental conditions described, Ni:Fe and Ni:Cu ratios were increased at least 100 fold, with a further 10 fold increase in solutions of higher acid concentration. The Ni:Zn ratio was increased over 2500 times, irrespective of acid concentration. No increase in the Ni:Co ratio was observed except in solutions containing greater acid concentration, where about a 3 fold increase occured. As expected, Ni:Al ratios were unaffected.

2.4.6 Preparation Of Nickel Oxide From Nickel Chloride Filter Cakes.

The preparation of nickel oxide from the filter cakes was achieved with a method involving the precipitation of nickel hydroxide. A low temperature heat treatment was used to convert the hydroxide to oxide. With this method, the overall procedure was simple, the only reagent needed being sodium hydroxide solution. Figure 2.4 shows the scheme.

Preliminary experiments showed that washing of the hydroxide or oxide to be essential to remove excess sodium chloride. Samples of oxide resulting from a procedure which included no washing stage, gave nickel and sodium contents of approximately 40% and 20% respectively.

Because of the gelatinous nature of nickel hydroxide, the washing procedure was carried out on the oxide.

Nickel chloride solutions, containing 125-135g/l Ni, and varying in purity depending on the prior treatment, (see 2.4.4 and 2.4.5), were treated with with a stoichiometric quantity of 4M NaOH solution, to completely precipitate the nickel content as hydroxide. Precipitation was done gradually, at 90°C with continual stirring, and the mixture then boiled for 15 minutes. The precipitate was filtered, and then heated at 400°C for 1 hour. The resultant oxide was powdered to 20 mesh, and stirred with an excess of hot water. The oxide was allowed to settle, and the liquor decanted. The washing procedure was repeated once and the oxide then filtered. Each oxide sample prepared, was dried at 80°C and analysed for metal content by A.A.S. Table 2.13 shows the results for % metal content of the oxides in terms of the observed range

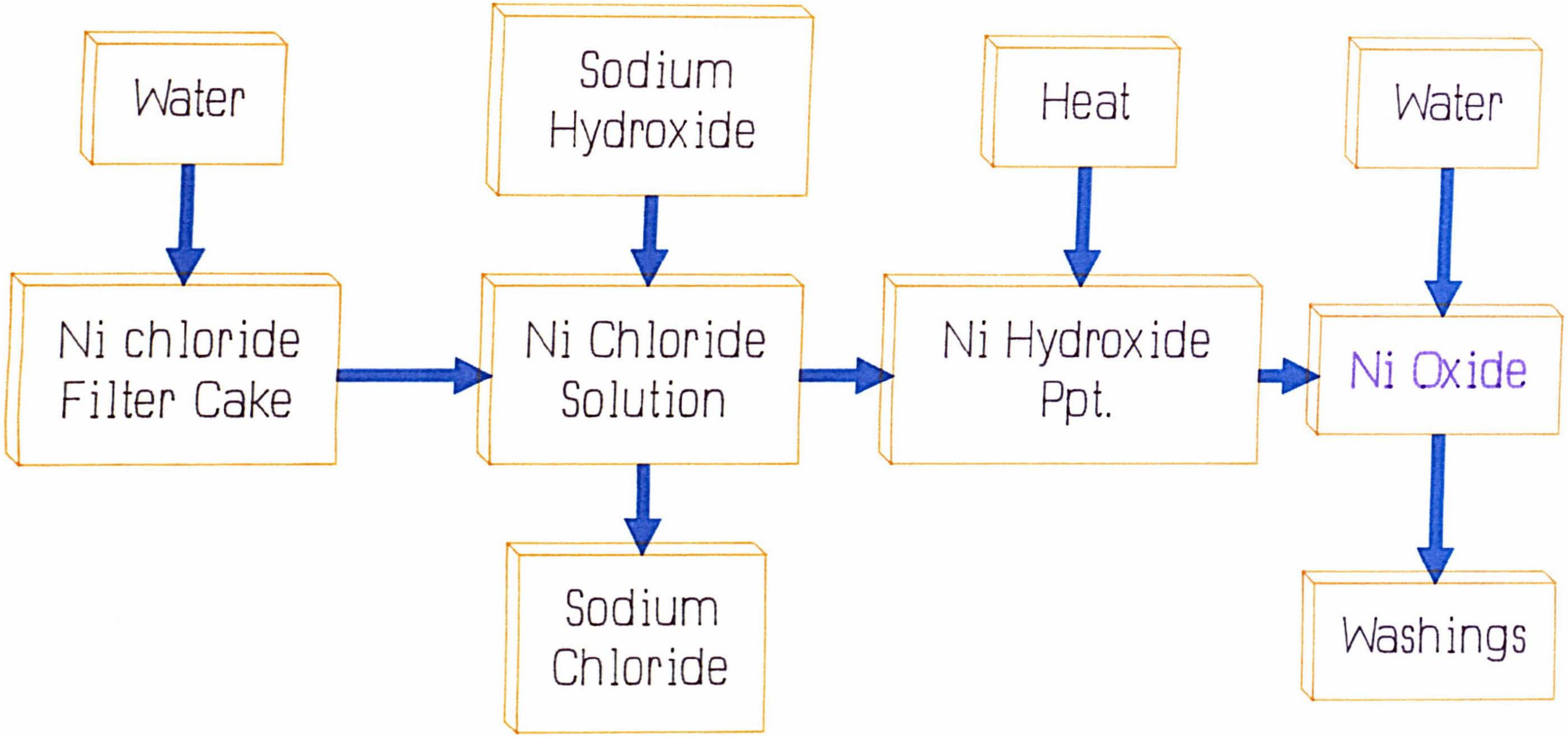

Figure 2.4 Nickel Oxide Preparation

for a series of products.

Table 2.13 Metal Content Of Products.

Pretreatment	Ni:secondary Metal Ratio	% Metal						
		Ni	Fe	Zn	Cu	Co	Al	Na
None	Typical of 3rd or 4th cycle ppt.	60 to 64	4.8 to 5.2	2.9 to 3.3	1.7 to 1.4	0.3 to 0.4	0.3 to 0.4	2 to 4
Filter Cake Washed Twice	Typical of Cake Washed Two Times	67 to 70	1.2 to 1.4	0.5 to 0.7	0.2 to 0.4	0.3 to 0.4	0.1	2 to 4
Anion Exchange	Typical of Solution Ex'd At pH 1.5	69 to 72	0.01	<0.01	<0.01	0.3 to 0.4	0.3 to 0.4	2 to 4

Negligible concentrations of Cd, Sn, Pb, Mo and Ca were found.

Table 2.13 shows that even with no pretreatment, an oxide was prepared containing >60% Ni, which is within the 50% specification. Furthermore, concentrations of secondary metals did not exceed the specifications given in table 2.2. However, with the introduction of a purification step, very low secondary metal concentrations were achieved, with a corresponding increase in the Ni content of the product - up to 10% compared with oxides from non-pretreated filter cakes.

2.4.7 Conclusions and summary.

The method detailed in the previous sections, involving the precipitation of nickel chloride and the subsequent preparation of nickel oxide, has been shown to be successful with respect to the overall purity of the oxide. Even with no purification of the precipitated nickel chloride, an oxide with an acceptable composition can be prepared, although results do suggest that with an increasing number of leach/precipitation cycles, (certainly in excess of 4), the combined copper and cobalt concentration of the product may become unacceptably high.

If a more stringent control of the impurity levels and the nickel content of the product is required, it has been shown that washing of the precipitate and/or the use of anion exchange, are an effective means of achieving higher purity. Very good results can be achieved using either purification method, allowing a flexibility in the coice of purification technique, depending on the purity target. Ni:secondary metal ratios can be considerably increased where Fe, Zn and Cu are concerned, but to increase the Ni:Co ratio is more difficult. However, the results do suggest, that a ratio similar to the Ni:Cu ratio will be obtained if anion exchange is used, and the HCl concentration of the solution to be treated, is increased from the 2M/l value used in the experimental work. Work by Kraus and Nelson [4], suggests a concentration of greater than 6M/l should be used for considerable purification from cobalt.

In order to increase the Ni:Al ratio, washing of the filter cakes is important, because Al^{3+} is an ion which is unable to form chloride anions in solution.

Washing of the nickel oxide is essential in order to achieve an oxide of acceptable Ni content. Indeed, in this respect, the overall sodium chloride content of the oxide is a limiting factor and depends on washing efficiency. To enable the washing stage to be as easy as possible, it is strongly recommended that washing should involve the oxide rather than the hydroxide because of the differences in the physical nature of the two compounds.

Accepting that in terms of results, the basic method described is successful, what are the main points of importance and interest which derive from the work?

a) Nickel chloride precipitation with HCl gas.

1) Complete saturation of the catalyst leachate with HCl gas is unnecessary; a satisfactory reduction in nickel chloride solubilty, at room temperature, can be achieved without saturation.

2) Complete precipitation of the nickel content of the catalyst leachate is also unnecessary, because residual nickel in solution after precipitation, is recycled. Thus an important flexibility in the quantity of HCl gas absorbed is present, negating the use of an accurate means to follow HCl absorption.

3) Precipitates obtained from the HCl treatment, are very easy

to filter and form compact, dry cakes of good handleability.

b) Repeated leach/nickel chloride precipitation cycles.

1) Recycling of solutions after precipitation, for use in the leaching of a fresh batch of catalyst, is possible. No disadvantage to nickel extraction, or extent of precipitation over 4 complete cycles, is apparent.

2) Recycling of solutions does have a detrimental effect on the purity of the precipitate. Continual recycling decreases Ni:secondary ratios.

c) Washing of nickel chloride filter cakes.

Washing of the filter cakes with concentrated hydrochloric acid, does solubilise a portion of the content. Problems associated with this fact, can be overcome by:

1) Returning nickel containing washings, (which are probably saturated with nickel chloride), to the leach stage - loss of nickel from the process in this way, is therefore avoided.

2) Minimising the number of washes, (and volume of washing solution), depending on the purity of the oxide desired.

d) Hydrogen chloride recycling.

The disadvantage of using HCl gas, where it is supplied commercially, is its expense relative to other common industrial gases. But the amount of gas required, can be minimised by:

1) Recycling HCl containing solutions.

2) Returning the HCl content of the filter cakes to the process.

In theory, HCl will only be inputed into the system to replace that consumed during catalyst leaching.

e) Overall nickel recovery.

Overall recovery depends solely on the efficiency of the catalyst leaching stage; a yield of approximately 75% is achieved based on the catalyst containing 17% Ni. Future work should therefore attempt to improve leaching efficiency with this type of catalyst. However, with a different catalyst, which contains a more easily leachable nickel content, the method described could be applied with even greater success.

f) By combining efficient filter cake washing with anion exchange, nickel chloride could be prepared with a purity of greater than 99.8%.

By taking into consideration the above points, a method for the recovery of the nickel value from the spent catalyst, can be finalised, and is outlined in the scheme given in figure 2.5.

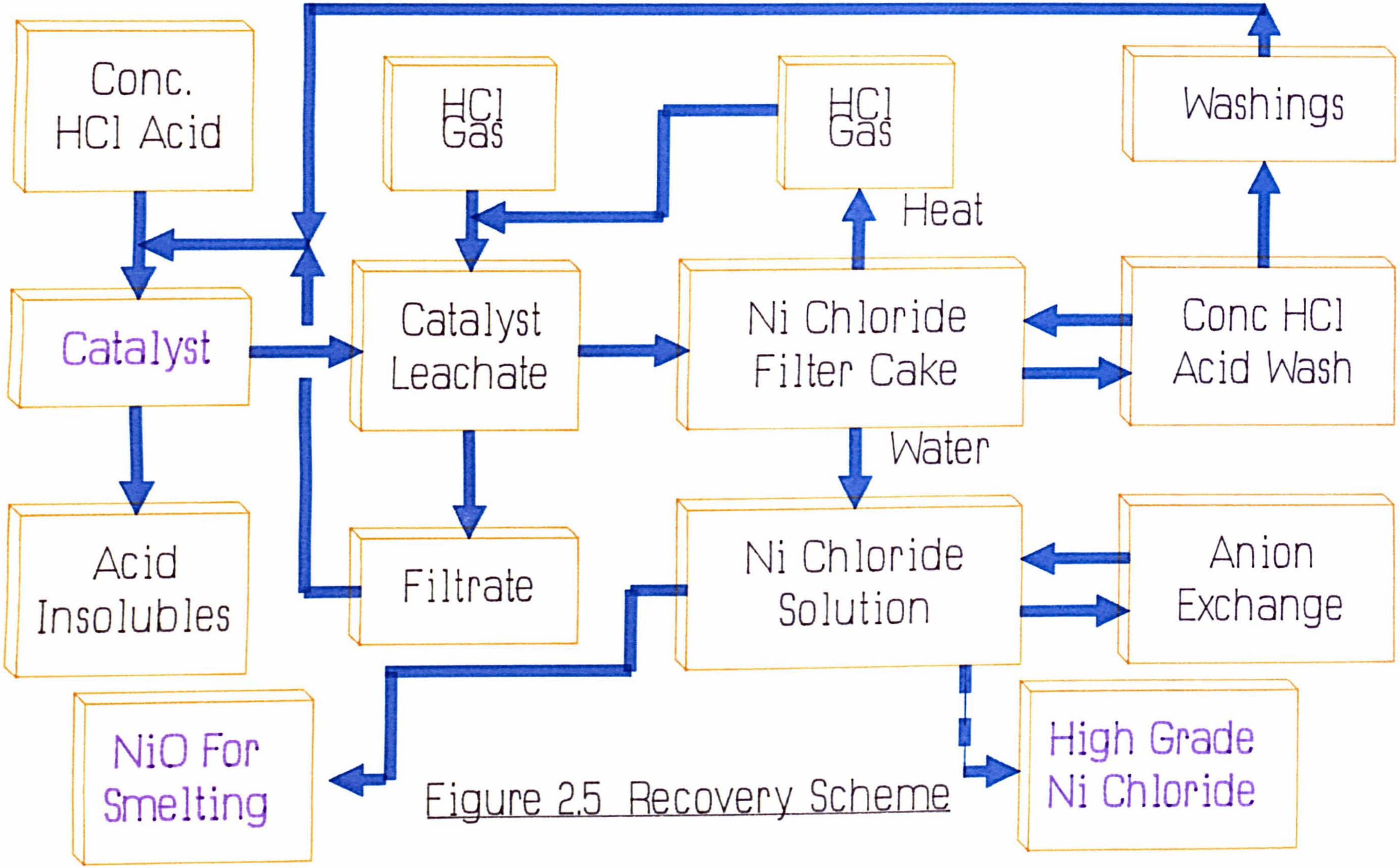

Figure 2.5 Recovery Scheme

2.5 Method 2 The Preparation Of A Concentrated Nickel Chloride Solution By Purification Of The Spent Catalyst Leachate.

2.5.1 Introduction.

In contrast to Method 1, Method 2 relies on the removal from the catalyst leachate of major secondary metals, to leave a concentrated solution which is purified to an extent to enable a nickel oxide to be prepared within the specification given in table 2.2. An outline of the proposed method is given in figure 2.6.

The effect on the nickel content of the product, of a major zinc impurity, is investigated by preparing a nickel oxide product both with and without prior treatment of the process solutions with an anion exchange purification step to remove the zinc impurity.

The preparation of nickel oxide from the purified nickel chloride solution is effected by the route described in Method 1 (2.4.6).

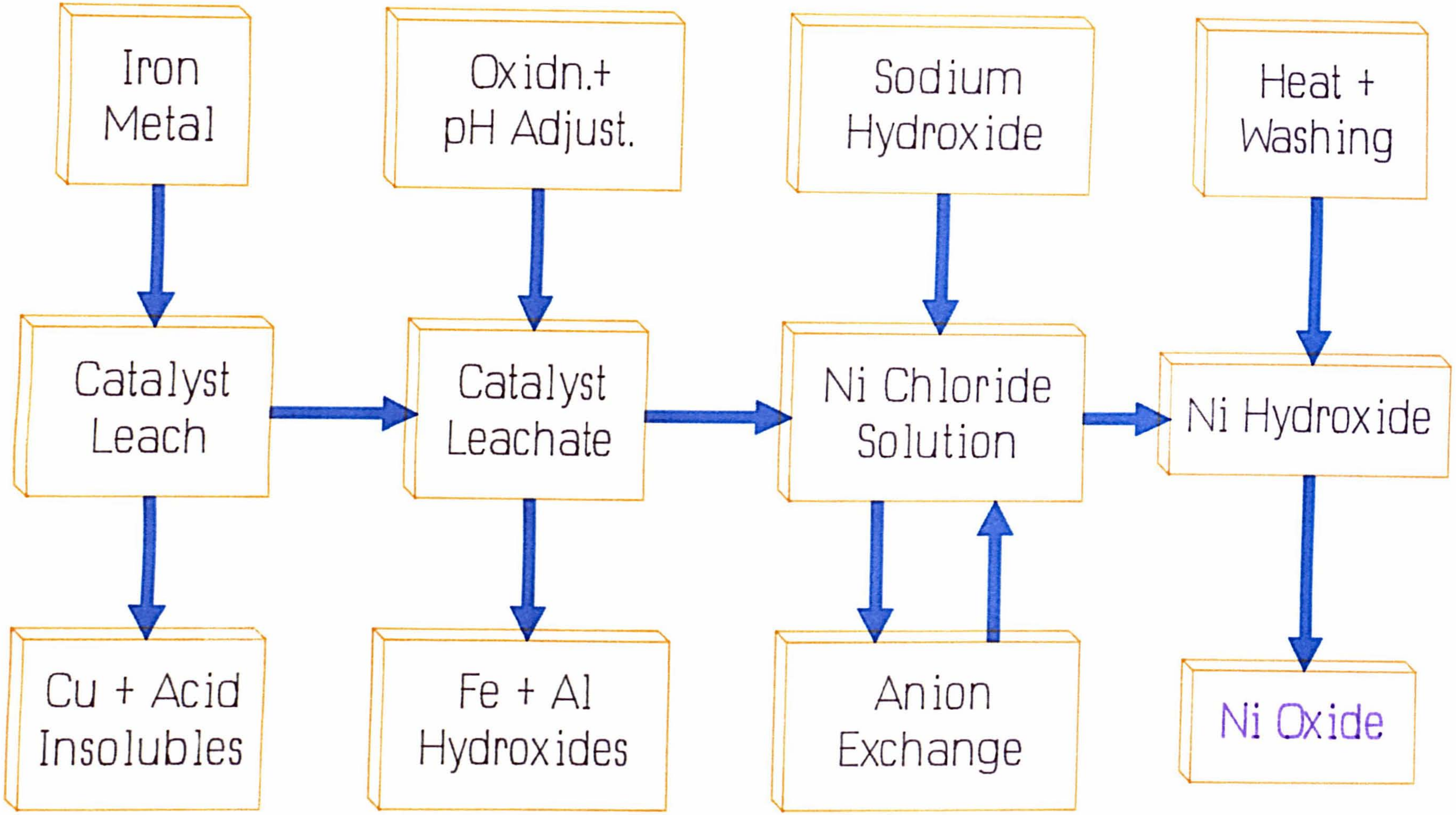

Figure 2.6 Proposed Scheme For Nickel Recovery

2.5.2 Leaching of the catalyst, and the removal of copper from the leach liquor by cementation.

The removal of copper from solution can be easily achieved by using a simple cementation reaction involving iron metal:

$$Fe + Cu^{2+} \text{ --------> } Cu + Fe^{2+}$$

This method could also afford a method of copper recovery by employing iron in the form of rods or plates from which the copper could be retrieved.

The solubilisation of quantities of iron via the cementation reaction, would not complicate the nickel recovery process, because significant quantities of iron would already be present in the catalyst leachate. However, in order to minimise the excess solubilisation of iron via an acid reaction, it was essential to allow the cementation reaction to occur in leach liquors that were low in acid concentration (>pH 1).

Preliminary experiments showed that if cementation was maintained at room temperature, and the iron was added in a massive form, rather than powder, (granulated and massive iron is relatively less reactive toward cementation than powdered form [8]. (See also section 3.4)), then negligible cementation of nickel occured.

200g samples of sieved catalyst were each leached with 320ml of 20% (v/v) hydrochloric acid. (An approximately stoichiometric quantity of acid). The leach mixtures were stirred for 4 hours with no external heating. After 1 hour, 10g of coarse iron filings were added. Following the 4 hour period, the leach mixtures were filtered, and the leachates analysed for metal content by A.A.S.

Table 2.14 shows the results of these analyses in terms of the range of concentrations found, together with typical Ni:secondary metal ratio values.

<u>Table 2.14 Leachate Analysis.</u>

	Ni	Fe	Zn	Cu	Co	Ca	Al
Conc. with Fe treatment (g/l)	65-69	25-27	8-10	<0.5	0.5-0.8	<0.07	0.6-1.0
Without Fe treatment (g/l)	65-69	20-22	8-10	4-6	0.5-0.8	<0.07	0.6-1.0
Typical Ni:M with Fe	-	2.5	7.4	200	105	1500	85

Leachate pH = 2.0 to 2.5 Volume of leachate = 89 to 93% of leach soln

Reference to table 2.14 shows that the copper concentration in the leachates was reduced considerably by the iron treatment - down to <0.5g/l. With the cementation technique, the Ni:Cu ratio in the leachates was reduced to a value calculated as being acceptable for the subsequent preparation of nickel oxide. (See table 2.2).

2.5.3 The removal of iron and aluminium from the leachate by pH adjustment.

The precipitation of impurity metal ions from solution by hydrolysis, caused by a controlled pH adjustment, is a common technique in hydrometallurgy used for the separation of certain secondary metals from the primary metal solution. Indeed, the removal of Fe^{3+} from solution as a hydroxy type precipitate, (Fe^{3+} can precipitate in a number of forms by hydrolysis [9], depending on conditions, such as geotite and jarosite [10,11]), is used in industrial operations.

The use of hydrolysis for the separation of iron from other metals in solution, is particularly attractive because of the very small solubility product of $Fe(OH)_3$ [12], allowing complete precipitation of Fe^{3+}, as $Fe(OH)_3$, at a pH between 3.0 and 3.5, a value which is decidedly more acidic than is found for the hydrolysis of the majority of metal ions. (Ni^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} undergo complete hydrolysis in the range pH 5 to 8 [13,14]. See figure 1.2).

In the context of the present work, the removal of iron from the catalyst leachate, (essentially a nickel chloride solution), would be a simple matter of adjusting the pH of the liquor following the treatment of the catalyst leachate with chlorine gas to ensure iron in solution exists wholly as Fe^{3+}. With this technique, it was suspected that a considerable proportion of the aluminium content of the leachate would also be precipitated by hydrolysis owing to the similarly low solubility product of $Al(OH)_3$. (Complete precipitation of $Al(OH)_3$ occurs above approximately pH 4, but to achieve this value in a concentrated nickel chloride solution would be difficult because of the problem of coprecipitation of $Ni(OH)_2$).

Catalyst leachates, pretreated to remove copper (2.5.2), were treated with chlorine by bubbling the gas slowly through the stirred solutions at 20-25°C. Complete oxidation of Fe^{2+} in solution was assumed to have been effected when the solution remained saturated with chlorine after cessation of the gas flow.

After the chlorine treatment, the solutions were heated to boiling, stirred vigorously, and the pH adjusted to approximately 3.5 with 4M NaOH solution. The hot liquor/precipitate mixtures were then filtered and each residue was compressed as much as possible. The filtrates were analysed for metal content by A.A.S. The range of concentrations found are given in table 2.15.

Table 2.15 Filtrate analyses after iron hydroxide precipitation.

	Ni	Fe	Zn	Cu	Co	Ca	Al
Conc. (g/l)	57-59	<0.01	0.5-7.5	<0.5	0.5	0.2	0.05
Ni:M Ratio	-	>7000	apprx 8	200	110	290	1150

The results show that the combined oxidatio/pH adjustment step reduces the iron and aluminium concentrations to low levels.

2.5.4 The preparation of nickel oxide from the purified nickel chloride liquor.

The procedure described in section 2.4.6, was used to prepare samples of nickel oxide from the treated leachates (60g/l Ni @ pH 3.5):

a) With no further treatment of the liquor.

b) With treatment of the liquor by anion exchange using Amberlite IRA-400 to remove zinc from solution. (See section 2.4.5).

Table 2.16 shows the ranges of metal concentrations found by A.A.S in the nickel oxide samples.

Table 2.16 Metal Content Of Nickel Oxide Samples.

	Metal Content (%)							
	Ni	Fe	Zn	Cu	Co	Ca	Al	Na
No Exch' Treatment	62-65	<0.01	6-8	<0.3	0.4-0.6	0.2-0.3	<0.1	2-4
With Treatment	68-71	<0.01	0.001	<0.3	0.4-0.6	0.2-0.3	<0.1	2-4

The results show that the purity of the oxides prepared were within the specification given in table 2.2. The samples were subjected to EDAX analysis, (see Appendix 2), which showed that negligible concentrations of Cd, Pb, Sn and Mo were present.

2.5.5 Conclusions and summary.

Table 2.16 shows that a nickel oxide of sufficient purity to meet the specifications given in table 2.2 can be prepared by the method proposed in figure 2.6.

With an anion exchange purification step to remove zinc from the nickel chloride solution immediately prior to hydroxide precipitation, an increase in nickel content in the oxide of about 6% from 62-65% to 68-71% can be achieved. The use of anion exchange in this way is ideally suited because complex zinc chloride anions are a species very easily absorbed by an anion exchange resin, requiring no control of solution acidity [15].

In conclusion, Method 2 relies on relatively simple procedures, such as pH adjustment and the application of anion exchange resins, (techniques already in common use in industry), and the minimum of reagent input, but can achieve satisfactory results for the preparation of a smelting grade nickel oxide from the spent catalyst. The method could provide for copper recovery if necessary.

With respect to yield, the same comments made about Method 1 are applicable to Method 2, i.e. the main factor governing the overall yield is the initial leach efficiency. (See 2.4.7).

2.6 A Comparison Of The Two Methods - General Conclusions.

From a purely subjective viewpoint, what would be the advantages and disadvantages of each method if expanded to an industrial scale?

Although each method relies on a totally different approach to the recovery project, both methods were developed with common aims, viz:-

a) To involve the minimum of stages within the process.

b) To use the minimum of reagents, with reagent recycling if possible.

c) To use simple, manageable techniques.

With these aims in mind, the processes have been given a firm foundation, in terms of practical and economic viability, if considered for industry. Overall, these constraints have been adhered to, but in terms of the cost of reagents, Method 1, the process involving hydrogen chloride gas, may be at a disadvantage. However, the method is ammenable to reagent recovery and recycling.

From the practical standpoint, the use of concentrated, probably fuming hydrochloric acid solutions throughout most of Method 1, would pose more problems on scale-up of the methods to industry, while Method 2 applies techniques commonly employed in industrial hydrometallurgical operations - an obvious advantage.

A factor which plays an important role in the degree of success of a particular recovery operation in industry, is the flexibility of the method regarding the composition of the raw material feedstock. With this factor, the concept involved in the recovery project is very important. If the process relies on liquor purification, leaving a solution containing only the primary metal, as in Method 2, with separate purification stages for specific impurities, then the introduction of a new contaminant to the feedstock may result in the need for the introduction of further process stages to maintain product purity, and therefore its suitability for the market outlet. However, if the recovery concept involves the precipitation of the primary metal value from the process solution, as in Method 1, then the problems discussed above are less likely to occur, provided the precipitation technique is reasonably specific.

With the above comments in mind, Method 1 would have an advantage if scaled up to industry. However, the final decision as to the suitability, would not only depend on the factors described, but also how well each method would integrate with existing on-site operations and resources.

In conclusion, both methods have been shown to be successful for the preparation, on a laboratory scale, of a smelting grade nickel oxide from a low grade spent nickel catalyst, and therefore foundations for the development of two industrial operations have been laid.

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CHAPTER 3

AN INVESTIGATION INTO THE USE OF NON-CONVENTIONAL ZINC RESIDUES IN THE ZINC CHLORIDE PROCESS AND THE RECOVERY OF THE COPPER VALUE FROM SUCH RESIDUES.

List of Tables and Figures

Figure Content Page

3.1 Introduction.

Zinc chloride is produced on an industrial scale in the U.K. by William Blythe & Co. Ltd. The zinc chloride is sold as a concentrated solution, (46, 58 and 72% w/w), and as an anhydrous powder, for use in many industrial and commercial outlets, including:

1) In pesticides as a timber preservative.

2) In the chemicals industry, for example in the manufacture of fluxes, diethyl zinc catalysts in the polymer industry, and as a process chemical in the manufacture of insulin.

3) In textile finishing for flame proofing, and as a mordant.

4) In the printing industry, in chemicals for etching lithographic plates.

5) In the electronics industry as a dry battery electrolyte.

6) As a corrosion inhibitor.

The raw material used by William Blythe for zinc chloride production, is a secondary zinc residue, consisting of zinc oxide fumes, zinc ashes and fines, and various other residues. The residue originates from the metallurgical industry, and is a by-product of various smelting and refining operations. The residue most often used in the zinc chloride process, (described in this work as the conventional zinc residue), consists of about 65% Zn, as a mixture of metal and oxide. It contains quantities of impurity metals, Fe, Cu, Mn, Al and Pb, generally in percentages of <2%. (Table 3.1). Sulphate is also a common impurity.

The zinc chloride manufacturing process, which is a batch

Table 3.1 Composition Of Conventional Zinc Residue.

Metal	Zn	Fe	Pb	Cu	Al	Mn	SO
%wt.	60-70	0.5-1.5	0.5-1.5	<0.1	<0.3	<0.05	<0.1

operation involving 2-3 tonnes of residue per batch, can be divided into three distinct process stages, (figure 3.1), viz:

a) Acid killing - treatment of the zinc residue with hydrochloric acid to give an impure zinc chloride solution.

b) Clearing - clearing the solution of major impurities.

c) Zinc dusting - final refining.

Acid killing.

A volume of concentrated HCl, (36% w/w), mixed with press washings from downstream operations, is added to a batch of zinc residue. The reaction is exothermic and no external heating is required. When the reaction is completed, the pH is between 1 and 3. The mixture is filtered to give a "black filter press" residue, (which is washed twice), and a concentrated liquor containing 30 to 40% $ZnCl_2$.

Clearing process.

The filtered liquor from the killing process is concentrated to about 46% $ZnCl_2$ by evaporation, during which time sodium chlorate is added to completely oxidise the iron in solution to Fe^{3+}. The pH of the liquor is then adjusted to approximately 3.5 to precipitate Fe^{3+} and Al^{3+} as hydroxides.

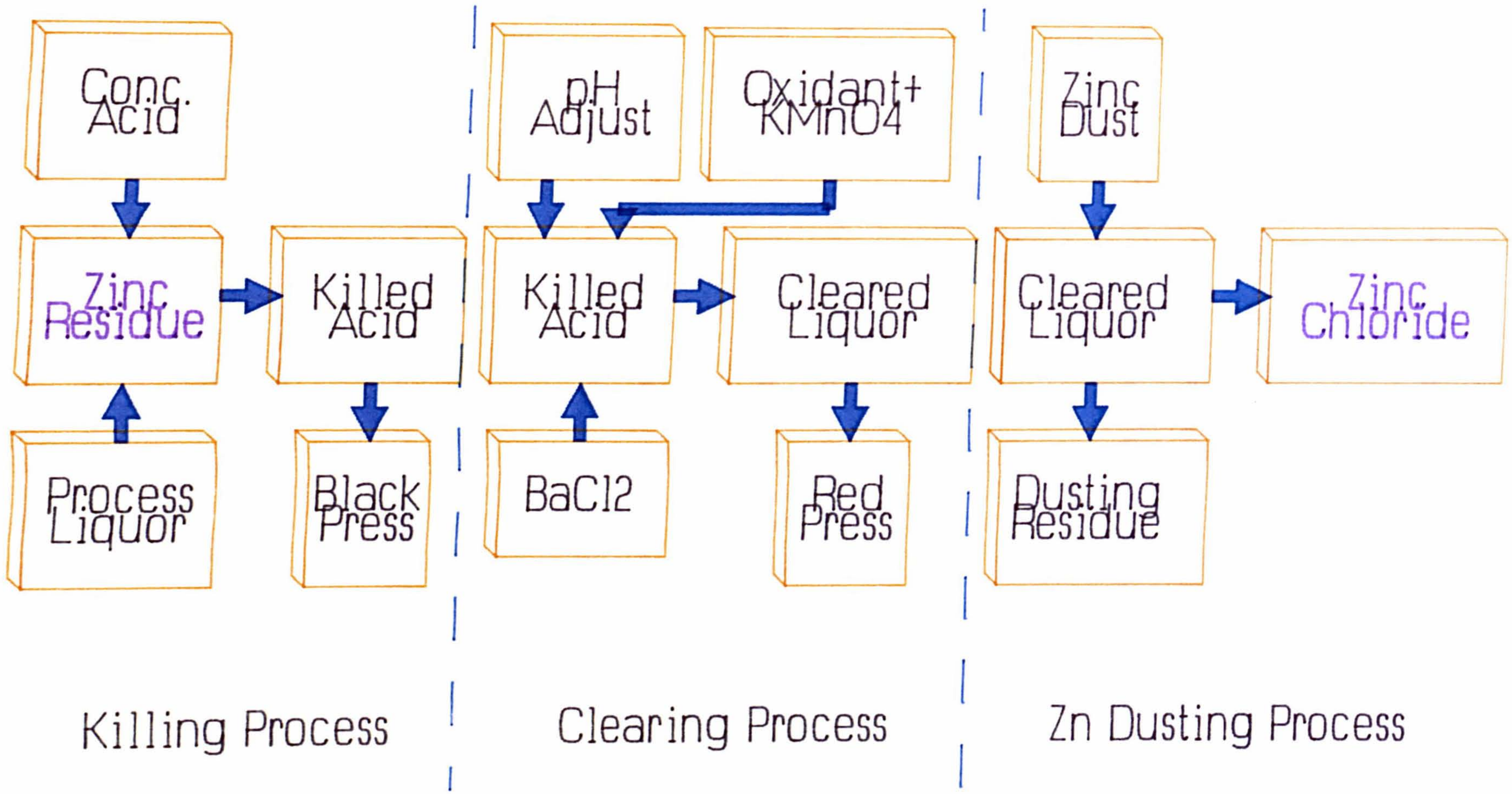

Figure 3.1 Scheme For Zinc Chloride Manufacturing Process

If the liquor gives a positive test for sulphate, sufficient $BaCl_2$ is added to precipitate all the sulphate as $BaSO_4$.

The liquor is then treated with $KMnO_4$ to precipitate manganese from solution as MnO_2.

Finally the mixture of liquor and precipitated impurities is filtered to give a "red filter press" residue, (which is washed once), and a concentrated $ZnCl_2$ solution which contains lead as the only major impurity.

Zinc dusting process.

The liquor resulting from the clearing process, is treated with zinc dust to precipitate lead and copper from solution. The precipitated metals are filtered off, and the filtrate is either evaporated to dryness under vacuum to produce anhydrous $ZnCl_2$, or concentrated to give 46, 58 or 72% w/w solution.

The process described produces $ZnCl_2$ of a purity which is suitable for most industrial and commercial requirements. (Table 3.2).

Table 3.3 shows the improvement in purity of the product compared to the raw zinc residue, in terms of Zn : secondary metal ratios.

The process has proved, over the years, to be a successful operation in terms of both its chemical and economic viability. However, problems are encountered, (as with all manufacturing

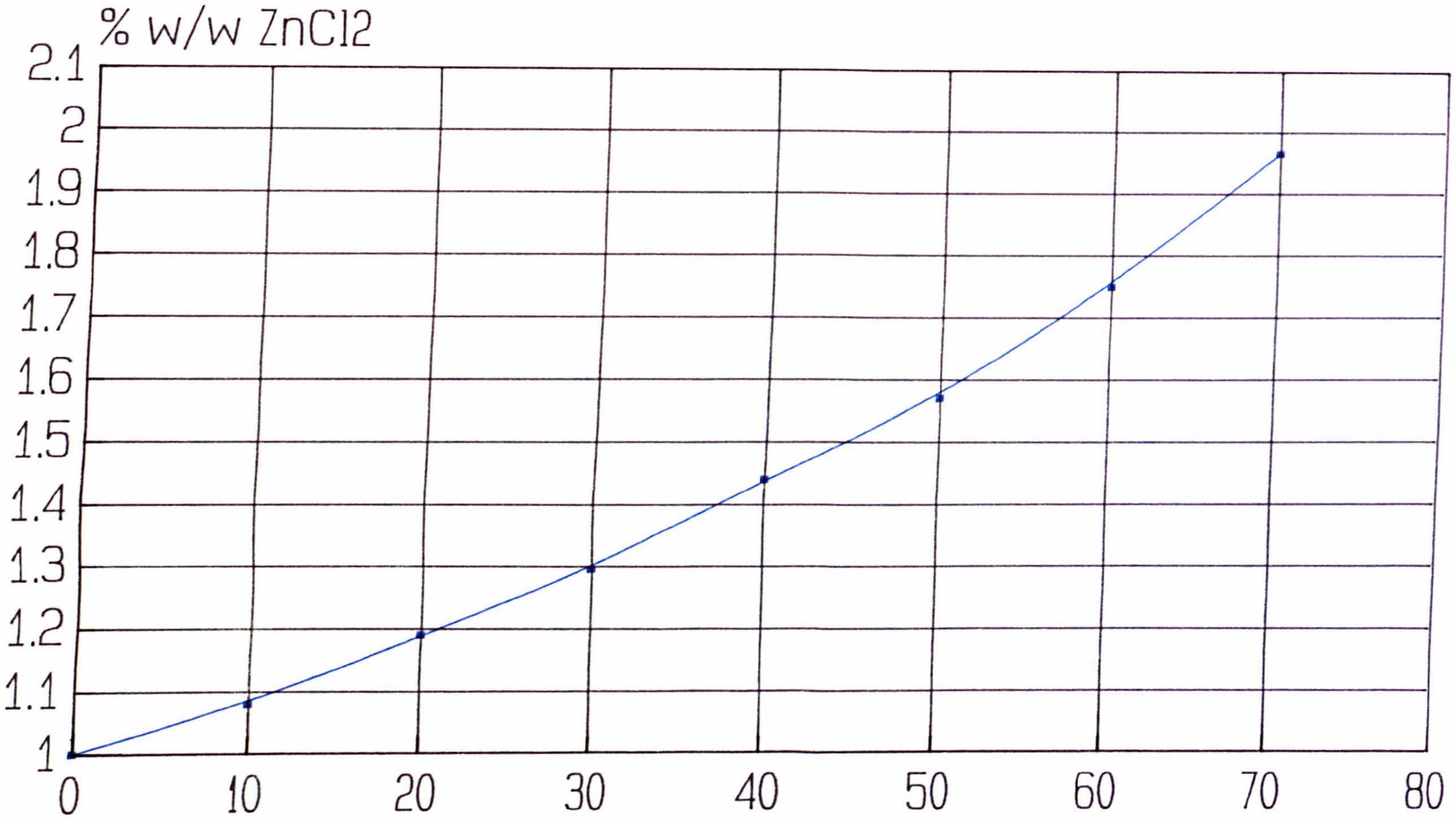

Figure 3.2
Specific Gravities Of Zinc Chloride Solutions At 20 C

Table 3.2 Technical Specification Of 46% $ZnCl_2$ Solution.

ZnCl	Zn	ZnO	Fe	Pb	Cu	Al	Mn
46%	22%	1.0%	<5ppm	<10ppm	<2ppm	<50ppm	<5ppm

Table 3.3 Comparison Of Raw Zn Residue And Product $ZnCl_2$

	Zn : Secondary metal ratio				
	Fe	Pb	Cu	Al	Mn
Zinc residue	65	65	1200	450	1600
46% solution	44000	22000	110000	4400	44000

processes), particularly with the availability of raw materials and reagents, and with fluctuating market demand for the product.

The largest area of concern at the present, is the problem of availability of residues which are suitable for the current zinc chloride process. Of specific concern is the presence of undesirably high concentrations of impurities in the feedstock. This applies particularly to the levels of Al, Cu and sulphate.

The current process can cope with higher levels of sulphate, but the larger amounts of $BaCl_2$ required to remove the sulphate results in a considerable increase in production costs.

The presence of unusually high concentrations of Al and Cu however, have direct effects on the chemistry and economics of the process. These effects arise from filtration difficulties and zinc dust consumption, respectively. These problems have usually been overcome by placing strict specification limits on the impurity contents of the residue feedstock. These restrictions however, necessarily reduce the choice of arisings available for use in the zinc chloride manufacturing process.

The aims of the work described in this chapter are to investigate:

1) The problem of a high Al impurity in the zinc residues, to enable these high Al residues to be used in the zinc chloride process without disadvantage.

2) The chemical behaviour of residues containing high concentrations of Cu, with a view to their use in the process, and to the recovery of the copper value.

3) The use of iron metal to remove Pb and Cu from a zinc chloride solution, as an alternative to purification with zinc dust.

3.2 A Method For The Use Of High Aluminium Zinc Residues In The Zinc Chloride Process.

3.2.1 Introduction.

In the process described in figure 3.1, any Al impurity present in the leachate is removed , together with the Fe impurity, simply by altering the pH of the liquor to precipitate these impurities as hydroxides. This method of separation works well with leachates which contain relatively small concentrations of Al, but the filtration of larger quantities of hydroxide presents a problem because of the gelatinous nature of the precipitate. [1,13]. To avoid these filtration difficulties, William Blythe impose a maximum Al content of 0.3% on the zinc residues used for zinc chloride production. So far, this necessary restriction on Al content has not caused problems with the availability of suitable zinc residue feedstock. The forecast on the future availability of zinc residues sufficiently low in Al however, indicates that problems may be encountered. Even at the present time, changes in techniques in the metallurgical industry result in zinc residues, containing higher percentages of Al, (often in excess of 3%), becoming available, replacing the available tonnages of residues which meet the specification limit.

The work carried out in this section of Chapter 3, describes a method of removal of Al based on the low solubility of aluminium chloride in concentrated zinc chloride solutions, saturated with HCl gas.

As Pb can often be a major impurity in zinc residue leachates, the effect of HCl saturation on the solubility of $PbCl_2$ in concentrated $ZnCl_2$ solutions, is also investigated.

The $ZnCl_2$-HCl-$AlCl_3$ system is investigated involving a study of:

a) The amount of HCl required to saturate $ZnCl_2$ of varying concentration, and

b) the variation of $AlCl_3$ solubility in such solutions.

The results obtained from these investigations are then used as a basis of a modification to the $ZnCl_2$ manufacturing process, to show that high Al zinc residues can be used succesfully for $ZnCl_2$ preparation, at least on a laboratory scale.

3.2.2 The use of hydrogen chloride gas to reduce the solubility of aluminium chloride in concentrated zinc chloride solutions.

In chloride solutions, many metals are present as anionic chloride complexes, a fact which is often utilised in the removal of metals from hydrochloric acid solutions, by anion exchange. (See section 4.3).

Certain metals, such as nickel, aluminium and the Group 1 and 2 metals, do not however, form anionic chloride complexes readily. The fact that Ni^{2+}, for example, forms only weak complexes with chloride ions, has been used in this work, as a basis for its separation from other metals in solution by the method described in the previous chapter. The method involved the saturation of $NiCl_2$ solutions with HCl gas, which resulted in the precipitation of nickel chloride, while other metals, which are able to form chloride complexes, remained in solution. Bearing in mind that the solubility of nickel chloride can be considerably reduced in this way, the possibility of separating aluminium chloride from a $ZnCl_2$ solution, using a similar technique, was studied.

A preliminary experiment involving the saturation, with dry HCl gas, of an unfiltered mixture of high Al zinc residue leachate, showed that aluminium chloride could be precipitated. In this case, the Al concentration was reduced from 12mg/ml to 0.4mg/ml, which is equivalent to a leachate derived from a zinc residue containing 0.1% Al.

3.2.3 Evaluation of the amount of hydrogen chloride gas required for the saturation of zinc chloride solutions of varying concentration.

Solutions of $ZnCl_2$, (prepared from GPR grade reagent), varying in concentration from 30.0 to 67.5% w/w $ZnCl_2$, were saturated with dry HCl gas, in a covered vessel, at 22°C. Saturation was shown by the use of bubble indicators before and after the gas was passed into the solution. The HCl saturated solutions were then analysed for acid content by acid-base titration , using methyl red as indicator.

The results of this investigation are shown in table 3.4, and shown graphically in figure 3.3.

Table 3.4 Hydrogen Chloride Saturated $ZnCl_2$ Solutions.

$ZnCl_2$ (%w/w)	Vol.increase on sat.(%)	HCl in sat. soln.(%w/v)	HCl in sat. soln.(%w/w)
30	36.9	41.35	30.41
38.5	34.5	38.51	26.93
45	32.5	37.14	24.76
53	32.0	35.15	22.24
61	32.2	34.11	20.18
67.5	31.4	32.01	17.88

The results show that with increasing $ZnCl_2$ concentration,

1) the quantity of gas required for saturation decreased, and

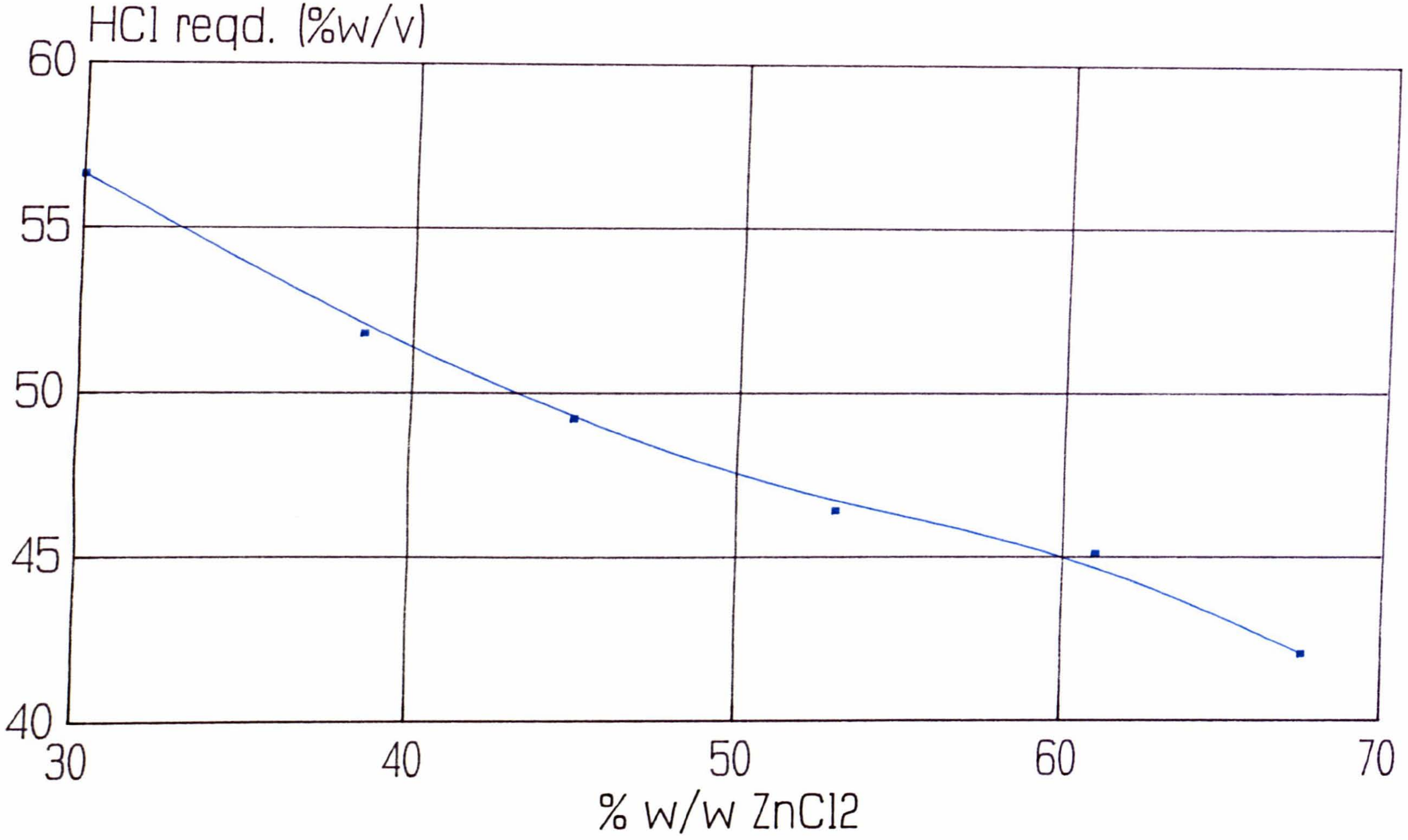

Figure 3.3
HCl Gas Required To Saturate Zinc
Chloride Solutions

2) the volume increase, resulting from the absorption of the gas into the solution, also decreased.

During the saturation of the solutions with the gas, no crystallisation was observed, which indicates a high solubility of $ZnCl_2$ in the HCl saturated solutions.

3.2.4 The solubility of aluminium chloride in $ZnCl_2$ solutions saturated with hydrogen chloride.

Solutions of $ZnCl_2$, varying in concentration from 30 to 67.5% w/w, were treated with dry HCl gas, until near saturation of the solutions was reached. Powdered anhydrous aluminium chloride was then added, in slight excess, to saturate the solutions with aluminium chloride. Further dry gas was then passed into the solutions until complete saturation with HCl was reached, at 22°C.

Each liquor/aluminium chloride slurry was stirred, with a magnetic stirrer, for 2 hours. A glass sintered filter, (No. 3 porosity), was then lowered into the liquor, and positioned so as to allow the solution to percolate up through the filter. Loss of HCl gas was minimised by keeping the vessel covered as much as possible. An aliquot of filtered solution was withdrawn and analysed for Al by a colorimetric method. (See Appendix 3).

The results are given in table 3.5 and figure 3.4.

It was found that the solubility of Al, as aluminium chloride, in the solutions, varied little over the concentration range 30 to 45% w/w $ZnCl_2$. Within this range, the solubility was found to be <0.06mgAl/ml. When the concentration was increased from 45%, the solubility increased sharply to reach a maximum of >14mgAl/ml in solutions containing 60 to 64% w/w $ZnCl_2$. The solubility then decreased in solutions containing greater concentrations of $ZnCl_2$.

Table 3.5 Solubility Of Aluminium Chloride In $ZnCl_2$ Solutions, Saturated With HCl Gas.

$ZnCl_2$ conc. before HCl satn.(%w/w)	Conc. Al in HCl satd. soln.(mg/ml)
30.0	0.02
38.5	0.03
45.0	0.05
53.0	0.39
54.0	1.28
57.5	5.70
61.0	14.60
64.0	4.60
67.5	3.60

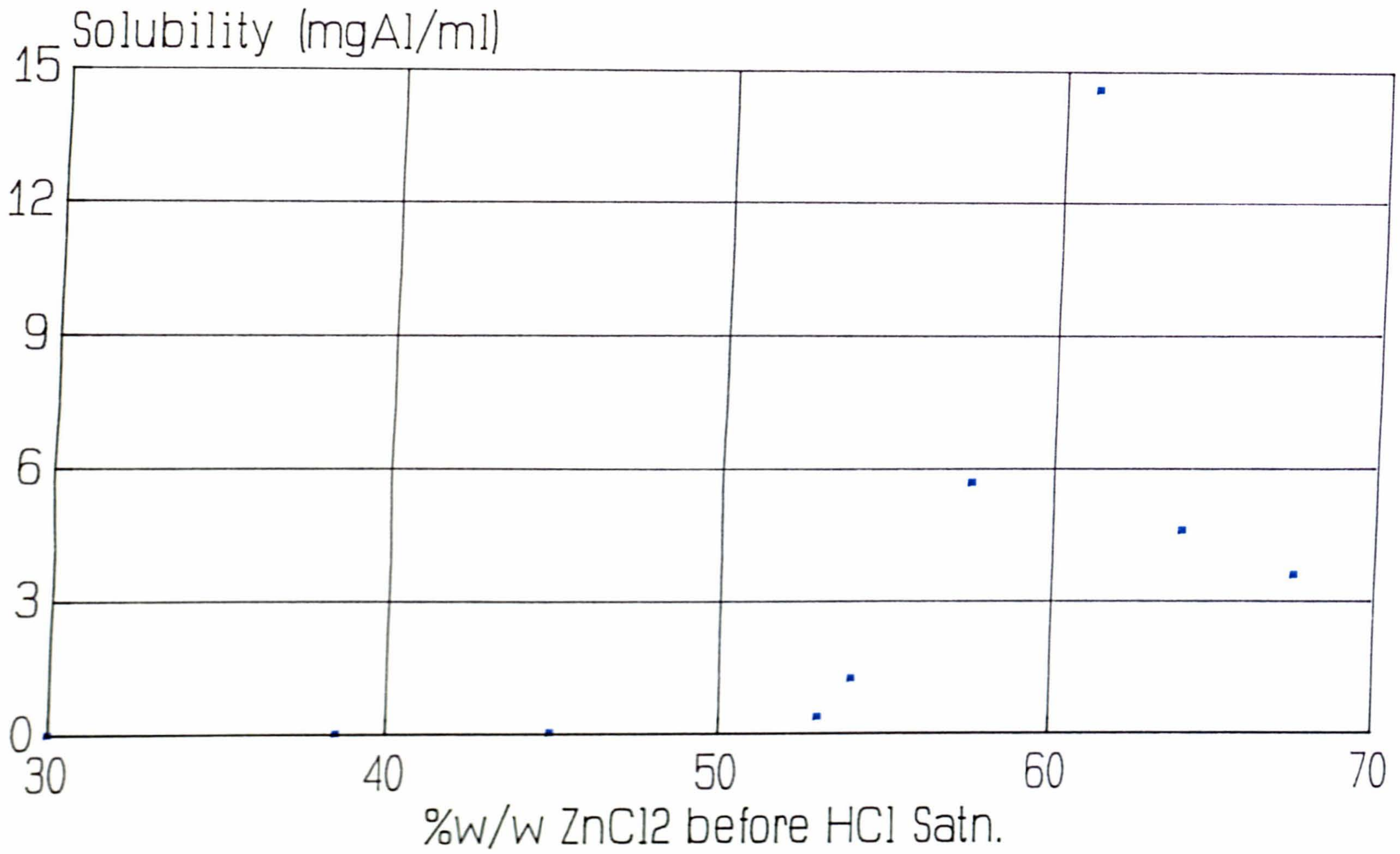

Figure 3.4
AlCl3 Solubility In ZnCl2 Solutions
Saturated With HCl Gas

3.2.5 The use of hydrogen chloride gas to reduce the concentration of Al in leachates deriving from high Al zinc residues.

The results obtained for the solubility of aluminium chloride in $ZnCl_2$ solutions saturated with HCl gas, show that it should be possible to control the $ZnCl_2$ concentration of leachates derived from high Al zinc residues to remove most of the Al as an aluminium chloride precipitate. By saturating the leachates with HCl gas, the Al concentration can be reduced to values less than the limits imposed for easy filtration of the treated leachates.

Conventional zinc residues generally require a weight of residue (g) : volume of solution (ml) ratio of about 1:2. Therefore, a conventional zinc residue containing 0.3% Al, (accepted as the maximum value for the process), would produce a leachate containing about 1.5mgAl/ml.

Reference to figure 3.4, shows that in order to reduce the Al concentration in the leachate to <1.5mgAl/ml, the liquor should have a $ZnCl_2$ concentration, prior to saturation with HCl gas, of <55% w/w, which corresponds to an S.G. of <1.65. (Figure 3.2).

Based on this information, the method involving HCl gas, was applied to leachates derived from high Al residues, with the aim of reducing the Al concentration in the leachates to an acceptable level.

200ml volumes of concentrated hydrochloric acid were treated with separate quantities of various high Al zinc residues until the pH of the liquors, in each case , was 1.0. The reaction mixtures, were cooled to 20°C, and sufficient concentrated hydrochloric acid was added to reduce the S.G. of the liquor to 1.47, a value corresponding to about 44% w/w $ZnCl_2$. Each unfiltered reaction mixture was then treated with dry HCl gas, until saturation. The gas treatment was carried out in a covered vessel, with continuous stirring of the liquor using a magnetic stirrer. When saturation was complete, stirring was continued for a further hour, and the liquor was then vacuum filtered using a glass fibre paper and the minimum of suction to avoid loss of HCl gas. The filtered liquors were subsequently analysed for Al concentration by A.A.S.

The results of these experiments are given tables 3.6 and 3.7, and show that when the leachates were saturated with HCl gas, the Al concentration in the liquor was reduced to within the 1.5mg/ml limit, from an initial concentration which varied from 17.7 to 6.7mg/ml. This means that treatment of the zinc residues which contained 2.5 and 1.3% Al, reduced the concentration of this impurity to an acceptable level for use in the $ZnCl_2$ process.

Comparison of the results for aluminium chloride solubility in HCl saturated liquors, show that the Al concentration in the leachates is higher than for a $ZnCl_2$ solution of similar concentration. In a 44% $ZnCl_2$ solution, aluminium chloride solubility is <0.05mgAl/ml, (figure 3.4), compared to a leachate value of 0.2 to 1.5mgAl/ml.

An explanation of this discrepancy, may be attributed to the type of filtration used for the leachates. With suction filtration, (which was not used when determining the solubility of aluminium chloride in

Table 3.6 High Al Zinc Residue Analysis.

Sample	Composition (%wt.)					
	Al	Zn	Fe	Pb	Cu	Mn
C1171	3.7	62.5	1.4	0.04	<0.01	0.03
C1171A	2.5	64.2	1.4	0.32	0.01	0.03
C1171B	1.3	63.8	1.3	0.51	0.01	0.04

Table 3.7 Effect Of HCl Gas On Leachate.

Sample	Wt.residue used (g)	Leachate		Acid added to adjust SG (ml)	Al conc.(mg/ml)	
		SG	$\%ZnCl_2$		Before	After
C1171	97.4	1.51	46.5	25	17.7	1.5
C1171	97.4	1.51	46.5	25	17.6	1.2
C1171A	98.0	1.52	47.0	33	12.0	0.4
C1171A	97.8	1.51	46.5	25	11.7	0.5
C1171B	106.3	1.54	48.5	46	6.7	0.2
C1171B	103.8	1.53	47.5	39	6.9	0.2

HCl saturated $ZnCl_2$ solutions), the conditions during filtration of the leachates, are not conducive to the liquor remaining saturated with HCl gas. Therefore, redissolution of some of the precipitated aluminium chloride is possible during the filtration procedure, which would give unexpectedly high concentrations of Al in the filtered liquor.

3.2.6 Application of the hydrogen chloride method to the zinc chloride process.

After treatment of the leachate with HCl gas, the liquor contains a high concentration of hydrochloric acid. To enable this leachate to be used in the $ZnCl_2$ process, the acid has to be neutralised. This can be achieved by dissolving quantities of low Al zinc residue in the liquor.

Leachates originating from the experiments described in section 3.2.5, were treated with conventional low Al residue, (batch 525, 0.13%Al), to use up the excess acid and alter the pH to 2. To avoid problems with high solution viscosity, the leachates were diluted with water, prior to the addition of zinc residue, to increase the volume by about 70%.

The leachates were cooled and filtered, and the filtrates analysed for metal impurity content by A.A.S. The approximate $ZnCl_2$ content of each filtrate was determined by measuring the S.G. The results are shown in table 3.8.

It was found that treatment of the diluted, HCl treated leachates, with low Al residue, resulted in $ZnCl_2$ solutions of similar S.G. and purity to a typical leachate deriving from a conventional low Al zinc residue. Of particular significance in the results, is the Al concentration, which is consistantly less than 1.5mg/ml.

Table 3.8 Treatment Of Leachates With Further Zinc Residue.

Sample	Dilution (ml)	525 res. added(g)	Liquor After Treatment								
			SG	$ZnCl_2$ (%)	Vol. (ml)	pH	Al	Fe	Pb	Cu	Mn
									(g/l)		
C1171	145	87.3	1.48	44	339	2.05	1.30	4.11	0.40	0.01	0.14
C1171A	160	95.1	1.47	44	384	2.20	0.59	2.53	0.92	0.01	0.12
C1171B	180	113.6	1.49	45	430	2.20	0.53	2.41	0.53	0.01	0.15
525	-	-	1.55	49	-	2.0	0.73	2.39	0.98	0.01	0.21

Data for 525, a conventional low Al residue, are derived from a single acid leach of this residue.

3.2.7 The solubility of lead chloride in zinc chloride solutions saturated with hydrogen chloride gas.

The experiment described in section 3.2.4, which investigated the solubility of aluminium chloride in zinc chloride solutions, saturated with HCl gas, was repeated for lead chloride, another of the impurities found in zinc residue leachates. The solubility of lead chloride in concentrated zinc chloride solutions at pH1 was also investigated for comparison.

The results are shown in figure 3.5, and tables 3.9 and 3.10.

Table 3.9 Solubility Of $PbCl_2$ In HCl Saturated $ZnCl_2$ Solns.

$ZnCl_2$ conc. (% w/w)	Solubility (mgPb/ml)
30.0	5.50
38.5	3.50
45.0	1.73
53.0	0.85
61.0	1.86
67.5	5.57

Table 3.10 Solubility Of $PbCl_2$ In $ZnCl_2$ Solutions At pH1.

$ZnCl_2$ conc. (% w/w)	Solubility (mgPb/ml)
30.0	0.96
38.5	0.72
45.0	0.62
53.0	0.64
60.0	0.65
66.0	2.01

The solubility of $PbCl_2$ in HCl saturated $ZnCl_2$ solutions was found to initially decrease when the concentration of $ZnCl_2$ was increased from a 30% solution, and reached a minimum at about 53% $ZnCl_2$.

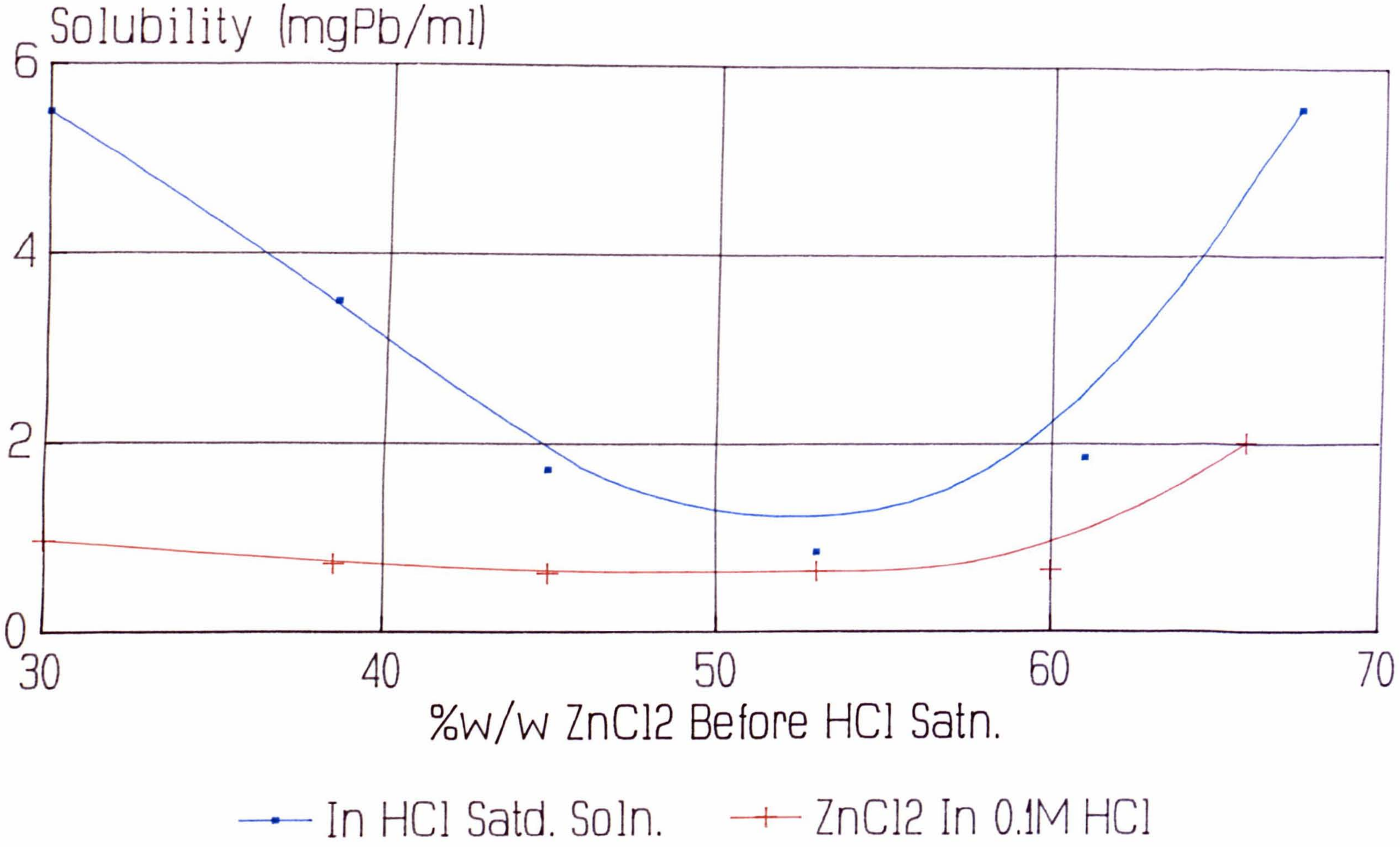

Figure 3.5
PbCl2 Solubility In ZnCl2 Solutions

The solubility was then found to increase steadily with increasing $ZnCl_2$ concentration.

Relatively little change in the solubility of $PbCl_2$ was observed with varying $ZnCl_2$ concentration in solutions at pH1, over the range 30 to 60% $ZnCl_2$

Figure 3.5 shows that the overall solubility of $PbCl_2$, in $ZnCl_2$ solutions, was found to be higher in those solutions saturated with HCl gas, over the range of $ZnCl_2$ concentrations investigated.

3.2.8 Conclusions and summary.

The work descibed has shown that the solubility of aluminium chloride in concentrated zinc chloride solutions, can be significantly reduced by saturating the solutions with HCl gas. The concentration of aluminium chloride can be reduced to less than 0.1mgAl/ml, from an original solubility in excess of 15mgAl/ml before the HCl treatment. However the solubility in the HCl saturated solutions, does depend on the $ZnCl_2$ concentration. The optimum concentration for maximum reduction in the aluminium concentration, is within the range 30 to 55% w/w $ZnCl_2$.

The solubility of $PbCl_2$ has been shown to increase in concentrated $ZnCl_2$ solutions when these solutions are treated with HCl gas. This fact is probably due to the formation of soluble anionic lead chloro-complexes. For lead removal, the optimum concentration is about 53% w/w $ZnCl_2$.

The application of hydrogen chloride gas for the removal of aluminium from high Al zinc residue leachates, has been shown to be successful; the solubility of aluminium chloride being reduced to <1.5mgAl/ml. This concentration of Al is equivalent to a leachate deriving from a low aluminium zinc residue. In an industrial situation, it would be satisfactory to use measurements of the specific gravity of the leachates as a means of optimising the concentrations prior to the HCl gas treatment. The high concentration of HCl in solution can be used up by addition of low Al zinc residue, to form additional zinc chloride. The final leachate would then have $ZnCl_2$ and aluminium chloride concentrations similar to those obtained by dissolving low Al zinc residue in hydrochloric acid in the conventional process.

A scheme that integrates the Al removal step into the industrial $ZnCl_2$ process is shown in figure 3.6. Three comments on the use of such a scheme can be made, viz:

1) The method permits the use of the high Al zinc residues that are being produced in increasing quantities, but still requires the availability of low Al residue.

2) No upper limit on the concentration of Al in the high Al zinc residue is imposed. The efficiency of aluminium removal depends only on the solubility of aluminium chloride in the hydrogen chloride treated leachate.

3) Hydrogen chloride gas is required for the precipitation reaction, but subsequently becomes a substitute for concentrated hydrochloric acid.

4) The quantities of low and high Al zinc residue required, are approximately equal.

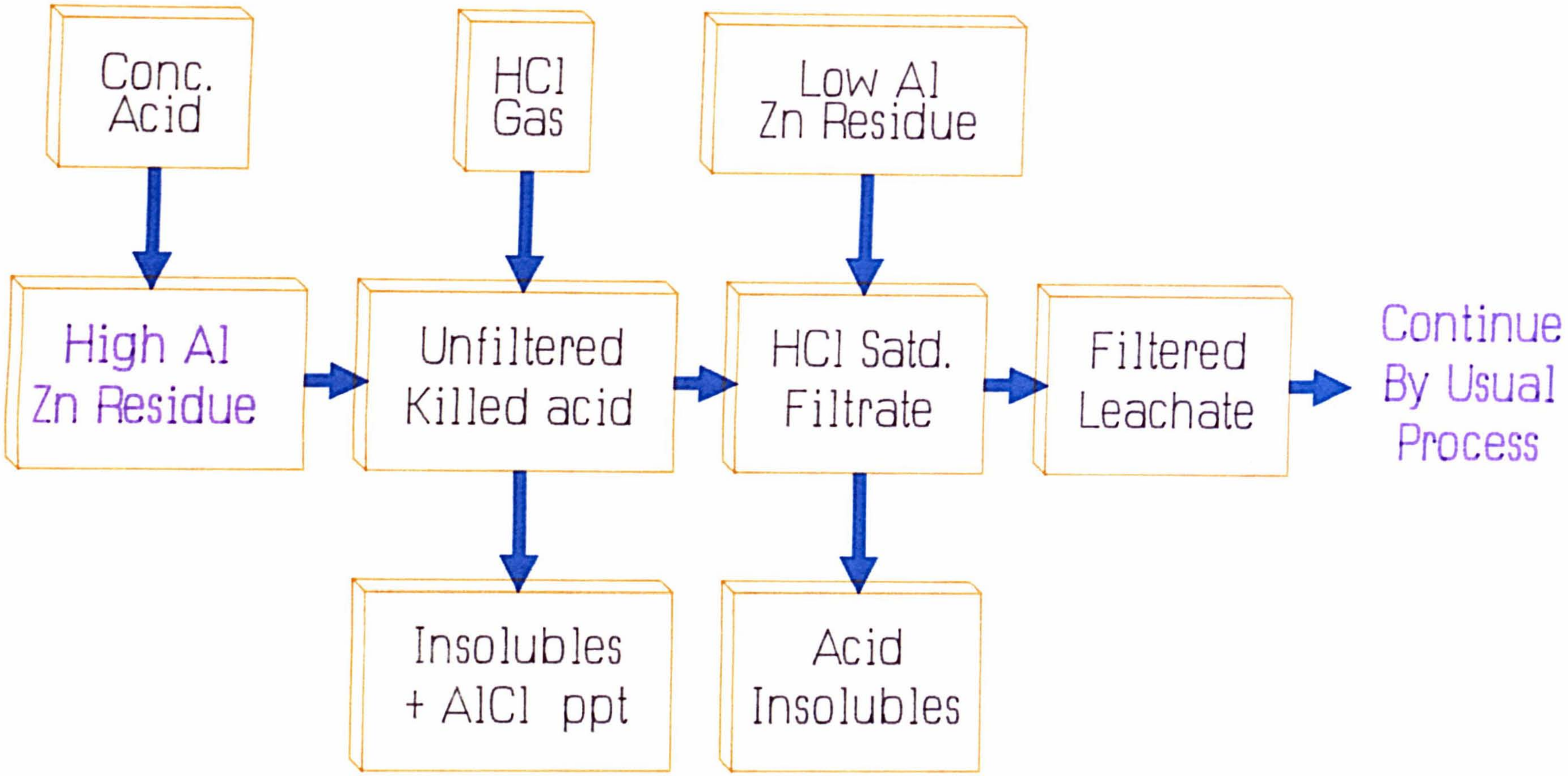

Figure 3.6 Scheme For The Integration Of The HCl Method Into The Zinc Chloride Process

3.3 The Recovery Of The Copper Value From High Copper Zinc Residues, And The Use Of These Residues In The Zinc Chloride Process.

3.3.1 Introduction.

Although the majority of zinc residues, and certainly those used conventionally for zinc chloride manufacture, generally contain only small quantities of copper, (<0.1%), there are residues available which contain considerable quantities of this metal, and which are available in tonnages large enough to permit their use for both zinc chloride production and copper recovery on an economic industrial scale. However, at the present time in the U.K., these high copper residues are not used for zinc chloride production, due to the lack of a suitable copper recovery process. The production of zinc chloride alone from these residues, would be economically unviable, because the residue price reflects both its zinc and copper value.

The following experimental work describes a method for the preparation of copper chloride from a high copper zinc residue. Copper chloride was chosen as the product of the recovery process, because this compound is already produced by William Blythe. The method which will be described, was designed from the outset, to allow the leachate, originating from the initial leach of the zinc residue, to be used directly for zinc chloride production by the established process. For reasons of economy, the incorporation of this feature in the process developed for zinc and copper recovery, is of prime importance if future use is to be made of the high copper residues on an industrial scale.

3.3.2 High copper zinc residues.

Samples of zinc residues, each containing a high percentage of Cu, were received from William Blythe. Table 3.11 shows metal analyses for each residue.

Table 3.11 Sample Analyses.

Sample	Zn	Cu	Fe	Pb	Al
			(Weight %)		
A	43.11	13.48	0.44	1.28	0.60
B	35.31	20.17	0.62	1.44	0.40
C1015C	24.4	54.6	0.36	2.70	0.06
C1015E	42.9	14.1	0.34	1.06	0.49
C1015F	34.4	25.4	0.50	1.80	0.34

Quantities of each sample were treated with a slight excess of concentrated hydrochloric acid, to give a liquor with a pH of between 0 and 0.5. After allowing the leach mixture to cool, (the reaction in each case was found to be very exothermic), it was filtered and the resultant leachate was analysed by A.A.S. The results of these analyses are shown in table 3.12.

As can be seen from table 3.12, very little solubilisation of the copper content of the zinc residues occured. Inspection of the leach residues showed they were composed of a considerable proportion of metallic Cu, a fact which explains the low concentration of solubilised

Cu in the leachates.

Table 3.12 Leachate Analyses.

Sample	Cu	Fe	Pb	Al	Dried leach res.
		(conc. g/l)			(% of sample)
A	3.21	3.85	0.59	0.26	53
B	0.60	3.41	0.36	1.08	69
C1015C	0.10	2.31	0.51	0.08	77
C1015E	0.07	2.14	0.50	1.01	39
C1015F	0.05	2.46	0.39	0.85	38

A semi-quantitative analysis of the leach residues, by EDAX (see Appendix 2), showed that each was composed mainly of Cu, with smaller quantities of Zn, Al, Pb and Si.

3.3.3 Recovery of the copper value, as copper chloride, from sample B high copper zinc residue.

Sample B was chosen for the investigation into copper recovery because apart from the high Cu content, concentrations of the secondary metals Fe, Pb and Al are similar to a conventional zinc residue used for the manufacture of zinc chloride.

3.3.3a Treatment of sample B with hydrochloric acid.

Quantities of sample were treated with concentrated hydrochloric acid to give a leachate of between pH 1.0 and 1.5. 100g of residue required 110ml of reagent. The leachate was found to contain impurities in concentrations comparable to those found in leachates deriving from conventional zinc residues. The leach residues, after filtration, weighed between 76 and 78g.

3.3.3b Solubilisation of the leach residue.

60g of leach residue was added to 115mL of water, acidified with 5ml of concentrated hydrochloric acid. Chlorine gas was passed into the stirred mixture until the copper metal had been completely solubilised. This was indicated by the change in colour of the liquor from dull green to a bright apple green, and the liquor becoming saturated with chlorine. The reaction was slightly exothermic and no heating was used. The cooled reaction mixture was filtered and the filtrate analysed by A.A.S.

A further 60g sample of leach residue was treated and analysed in a similar way with the exception that the sample was treated with two 60ml volumes of concentrated hydrochloric acid to solubilise the remainder of the leachable material. This was followed by a thorough wash of the residue with water, before the chlorine treatment as described. The samples of leach residue were found to be reduced to 45 to 50% in weight during this acid pretreatment.

The two procedures described were repeated with further samples of leach residue. The solutions so prepared were approximately 2M in copper chloride and 0.4M in HCl.

The residues from the chlorine treatment were 6 to 9% of the original leach residue. EDAX analyses of washed samples of these residues showed them to be mainly composed of Si, apparantely as a sand, with negligible concentrations of Cu.

Table 3.13 shows the range of Cu:secondary metal ratios found in the copper chloride solutions prepared as described.

Table 3.13 Copper Chloride Solution Analyses.

	Cu:secondary metal ratio				
Leach residue	Zn	Fe	Pb	Mn	Al
Non pretreated	1.3-1.4	70-110	17-24	280-400	90-110
Pretreated	2.0-2.6	230-270	40-50	4000	800

It was found that pretreatment of the leach residue, with the acid wash procedure, gave copper chloride solutions which contained Cu:secondary metal ratios considerably improved to those in solutions originating from non pretreated leach residues. Ratios were increased generally by 10 fold for Mn and Al, and 2 to 3 fold for Zn, Fe and Pb.

3.3.3c Purification of the impure copper chloride solutions by anion exchange.

Table 3.13 shows that the main impurities in the copper solutions are Zn and Pb. The removal of a zinc impurity from a chloride solution can be readily achieved by anion exchange, (see section 2.4.5), because anionic chloride complexes of Zn^{2+} are tenaciously retained by a strong base anion exchange resin, even from very dilute solutions of negligible hydrochloric acid content. [2,3]. Work by Kraus and Nelson, [18], showed that lead can also be removed from chloride solutions, of low acid content, by a similar technique.

Kraus and Moore [3], determined that in hydrochloric acid solutions, copper is retained by a strong base anion exchange resin, only if the overall chloride concentration, (as hydrochloric acid), is greater than 3M. Therefore, to purify the copper solution by anion exchange, it is apparent that the overall chloride concentration should be less than 3M, (i.e. for very dilute hydrochloric acid solutions, e.g. >pH1, where the chloride contribution is essentially only from the copper salt, the concentration of $CuCl_2$, should be <1.5M), if retention of copper by the resin is to be avoided.

The use of an anion exchange resin therefore seems to be an ideal method for the purification of the copper solutions from the major impurities. In this way, the recovery of the zinc value as a zinc chloride solution, may be achieved by elution of the loaded resin with water.

A sample of impure $CuCl_2$ solution, originating from a pretreated zinc residue, was diluted with an equal volume of water to give a solution containing 1.1mole/l $CuCl_2$, (68.2gCu/l), and 0.2mole/l HCl. This solution was then passed through an anion exchange column containing Amberlite IRA-400 resin, (chloride form). The resultant solution was then analysed by A.A.S. Table 3.14 shows the effect of the treatment on the purity of the copper solution, in terms of Cu:secondary metal ratios.

Table 3.14 Effect Of Anion Exchange On $CuCl_2$ Solution Purity.

	Cu:Secondary metal ratio				
	Zn	Fe	Pb	Mn	Al
Before	2.6	252	47	4000	800
After	>40,000	254	4000	4000	800

It was found that in all cases when further solutions were treated in the same way, similar results were obtained. Impurity levels of Pb, and particularly Zn, were decreased dramatically. As expected, no improvements for Fe,Mn and Al were observed.

3.3.3d Preparation of anhydrous $CuCl_2$ from the resin treated solutions.

The resin treated copper solutions contain typically 0.2M HCl. Before the preparation of the anhydrous salt, the acid needs to be neutralised. This can be conveniently achieved with CuO, which by raising the solution pH to above 3.2, would also serve to reduce the iron concentration in solution, (iron will be present as Fe^{3+}, because of the previous chlorine treatment), by precipitation of hydrolised Fe^{3+}, (section 2.5.3).

A sample of the resin treated copper solution, was heated to boiling and treated with CuO, (SLR grade), to raise the solution pH to approximately 3.5. The liquor was filtered and the filtrate evaporated to initiation of crystallisation. Complete crystallisation was effected by cooling. To convert the hydrated $CuCl_2$ to the anhydrous form, the crystalline mass was heated at 105°C for 3 hours. The purity of product was determined by analysis with A.A.S. The results of the analysis is shown in table 3.15

Table 3.15 Anhydrous $CuCl_2$ analysis.

	Cu	Zn	Fe	Pb	Mn	Al	Ca
Ratio	--	>47000	15000	>47000	20000	4000	6000
%	47.13 0.05	--	--	--	--	--	--
ppm	--	<10	30	<10	20	110	80

The results given in 3.15 were found to be typical of further samples of anhydrous $CuCl_2$ prepared in the way described. The Cu content of such samples varied between 47.08 and 47.20%, giving an assay for $CuCl_2$ of 99.6 to 99.9%. The theoretical Cu content for pure $CuCl_2$, is 47.26%.

3.3.4 Pretreatment of the leachate, containing solubilised copper, to precipitate the copper as copper metal.

In section 3.4 it will be shown that a concentrated $ZnCl_2$ solution, containing solubilised copper, can be treated with Fe metal to precipitate the copper from solution. In this way, the copper concentration can be reduced to less than 5mg/l. If massive Fe metal is used, and the solution is maintained at room temperature, the work in section 3.4 also shows that it is possible to precipitate the Cu from solution without precipitating Pb. The use of massive Fe, e.g. rods, allows separation of the Fe and precipitated Cu to be effected.

The method of precipitating Cu from $ZnCl_2$ solutions without coprecipitation of Pb, has an attractive application to the work described in the previous sections. Thus, where an unfiltered leachate, originating from a high Cu zinc residue, contains a significant concentration of solubilised Cu, the method described would provide a route to confining the copper content of the zinc residue totally to the acid insoluble residue, without contamination of the residue with unreacted Fe or precipitated Pb.

Sample A, described in section 3.3.2, is an example of a high Cu zinc residue containing a proportion of acid soluble Cu.

200ml of concentrated hydrochloric acid was treated with sufficient sample A to kill the acid to pH 0.9. The unfiltered leachate was cooled to 23°C, and 3.1g of clean Fe nails, attached to nylon lines, were completely immersed in the liquor, which was stirred vigorously with a magnetic stirrer. After 1 hour the nails were withdrawn, and the liquor filtered. The filtrate was analysed for Cu and Pb by A.A.S. both before and after the Fe treatment.

A further two samples of sample A were treated similarly. The results of these analyses are given in table 3.16.

Table 3.16 Treatment Of The Leachate With Massive Fe Metal.

Run	Cu conc. (mg/l)		Pb conc. (mg/l)	
	Initial	Final	Initial	Final
1	3190	33.1	507	510
2	3340	17.0	580	579
3	3305	21.4	611	606

The results show that the Cu concentration was reduced to concentrations which are comparable to those found in conventional zinc residue leachates, without a significant reduction in the Pb concentration in solution.

3.3.5 Conclusions and summary.

The method described for the recovery of the copper value, as copper chloride, from a high Cu zinc residue, has been shown to be successful.

The Cu content of each high Cu zinc residue received from William Blythe, was found to be mainly composed of metallic Cu, which resulted in little soluble Cu in the leachates. Thus, in theory, each of these high Cu zinc residues, could be treated with the same method developed for sample B for the recovery of the Cu value as copper chloride of commercial value.

It has been shown that high Cu zinc residues which give leachates containing a significant concentration of solubilised Cu, can still be used for Cu recovery, using the method described, by precipitating the copper with Fe metal. In so doing, the Cu content of the zinc residue is restricted to the leach residue, and the leachate contains a Cu concentration comparable to those deriving from conventional zinc residues.

Although the concentration of typical impurities in leach residues, would certainly differ, depending on the feedstock, the method developed for copper chloride manufacture, would be flexible with respect to variations in the concentration of most impurities in the leach residues. Pretreatment of the leach residue with hydrochloric acid, followed by residue washing, accounts for the majority of the leachable impurities. This pretreatment stage can be considered an important step in the production of a copper chloride of good purity. The presence of untypically large concentrations of Zn, Fe and Pb in solution could be dealt with, without any major change to the recovery route. Higher concentrations of Al could reduced to acceptable levels by ensuring on addition of the CuO, the pH is raised to at least 3.4 to coprecipitate the Al^{3+} with the Fe^{3+} in solution by hydrolysis. However, high concentrations of Mn may be troublesome.

In conclusion, the method described, provides a route for the production of good quality copper chloride, (>99.6% purity), from suitable high Cu zinc residues, while still enabling these residues to be used for zinc chloride production via the established process.

A high Cu zinc residue can be considered suitable for the recovery of both Zn and Cu value, via the route developed if:

1) The Cu content of the zinc residue is resistant to leaching with hydrochloric acid, but can be solubilised with a chlorine/acid combination. Ideally, the copper content should be metallic Cu.

2) The Cu content of the zinc residue is soluble only to a limited extent, to enable therefore, the precipitation of the Cu with massive Fe, without an excessive increase in the solution Fe concentration to an extent which will give problems in subsequent $ZnCl_2$ manufacture.

3) The leachate deriving from the high Cu zinc residue, is of a purity suitable for $ZnCl_2$ manufacture.

A scheme based on the work described, for the industrial manufacture of $ZnCl_2$ solution and anhydrous $CuCl_2$, from a high Cu zinc residue, of the types described, is given in figure 3.7.

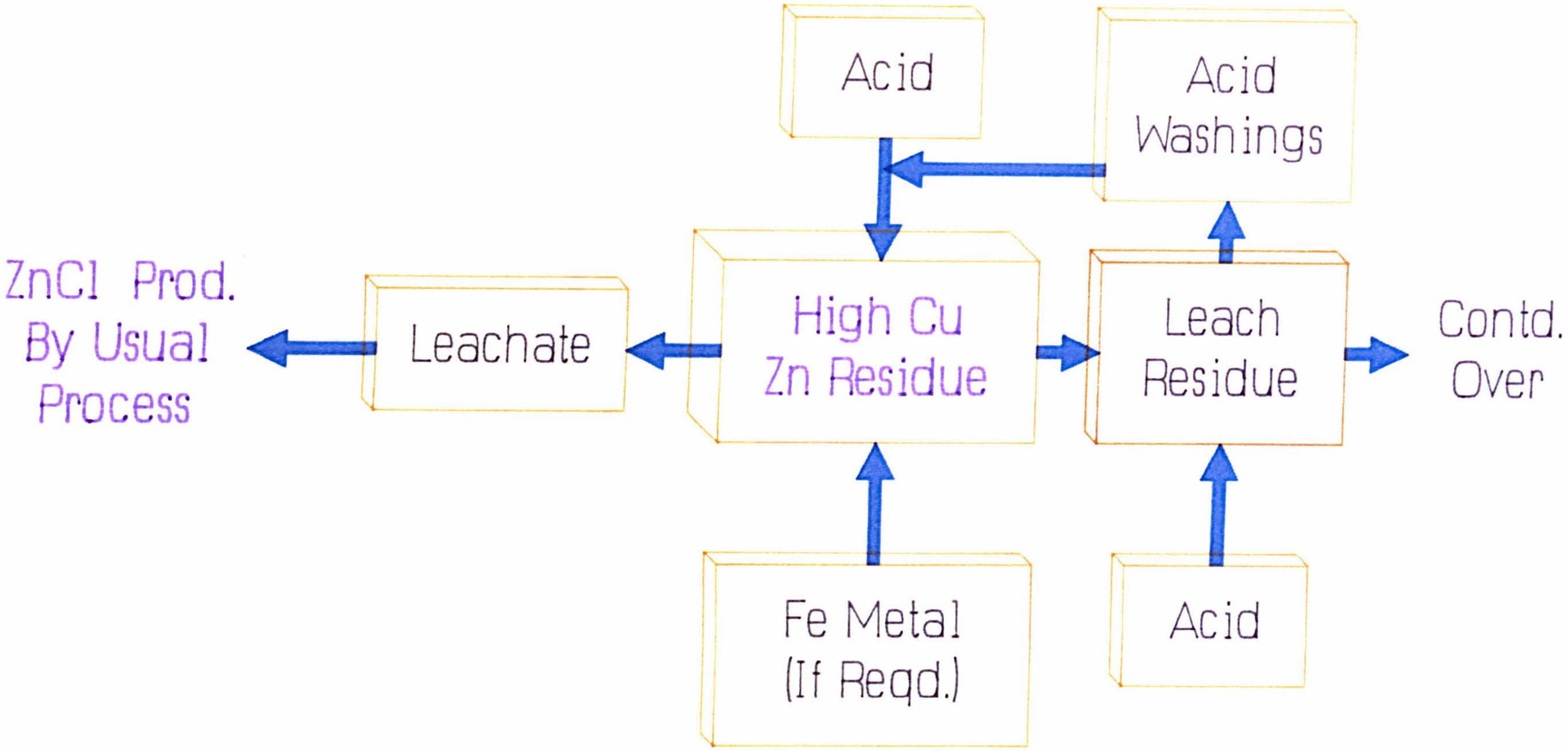

Figure 3.7 Scheme For The Recovery Of The Cu Value, As Copper Chloride, From A High Cu Zn Residue.

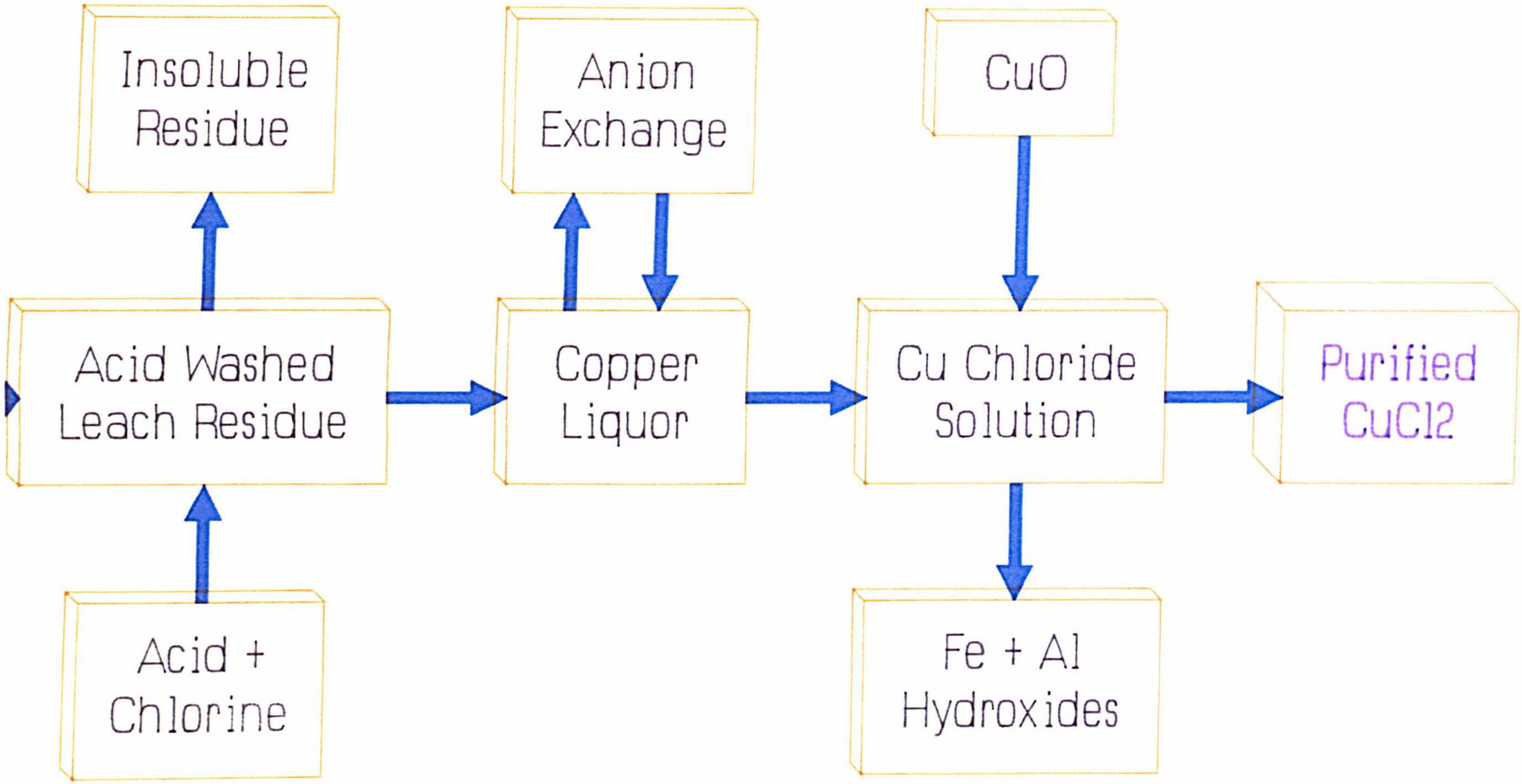

Figure 3.7 Continued

3.4 The Use Of Iron Metal To Reduce The Concentrations Of Lead And Copper, In Concentrated Zinc Chloride Solutions, By Cementation.

3.4.1 Introduction.

In the industrial manufacture of $ZnCl_2$, the lead impurity in the process solutions is removed by treatment of the solutions with Zn dust. (section 3.1).

$$Zn + Pb^{2+} \text{--------}> Zn^{2+} + Pb \qquad E = +0.63V$$

This treatment also serves to reduce the copper concentration in solution.

$$Zn + Cu^{2+} \text{--------}> Zn^{2+} + Cu \qquad E = +1.10V$$

This zinc dusting process has proved to be successful in the manufacturing process, but has the disadvantage of being an expensive treatment because of the cost of the reagent.

Iron metal has long been used, and is a well known reagent for the precipitation of Cu from aqueous solutions. [5,6,7,8]. Its uses for this purpose in hydrometallurgical processes, is especially popular because of the frequency in occurance of iron as an initial impurity in such solutions.

$$Fe + Cu^{2+} \text{--------}> Cu + Fe^{2+} \qquad E = +0.78V$$

The use of Fe metal for the precipitation of Pb from aqueous solutions, seems to have been investigated to a very limited extent, because literature references on this subject are scarce. The reaction is favourable,

$$Fe + Pb^{2+} \text{--------}> Pb + Fe^{2+} \qquad E = +0.31V$$

and would seem to be an attractive method for the purification of aqueous solutions from a lead impurity. It would be particularly favourable where an iron impurity in solution already exists, and where chloride solutions are involved. The use of sulphate or sulphide precipitation would probably be undesirable because of the introduction of these anions into solution.

In the context of the $ZnCl_2$ process, the use of cementation with Fe metal as an aid to, or even a replacement for, the Zn dusting stage, does seem attractive because of the apparent economic advantage of replacing partly, or even wholly, Zn dust with Fe metal.

Table 3.17 Cost Of Fe Powder And Zn Dust.

Metal	Cost (£/3Kg)
Zn Dust	13
Fe Powder	5

The experimental work described in the following sections of Chapter 3, investigates the use of Fe metal, both massive and powder, for the purification of concentrated $ZnCl_2$ solutions from lead and copper impurities.

3.4.2 Iron powders.

In any experimental work where metal powders are used, it is important to describe the nature of the powder. The powders of many individual metals, can be obtained in various forms, and can often be differentiated by the process of manufacture, which in turn, attributes the powders with a particular particle size distribution and density. [10,11,15]. This is certainly true of Fe powders, [12,16,4], which can be obtained in several different forms, the major preparative techniques for which are:

1) Atomization - A stream of molten metal is struck with air or water jets. The particles formed this way are collected and sieved. This is probably the most common method of production.

2) Reduction - Iron oxide is reduced in a solid or gaseous medium, to give sponge Fe or hydrogen reduced mill scale. The powder produced is usually the most impure of the powders. The powder has an average particle size of 6-70 microns, depending on the conditions.

3) Electrolytic deposition - Fe is deposited from aqueous solutions by electrolysis. By control of the reaction conditions, powdery deposits can be obtained. Fe powder produced by electrolysis, has an average particle size of 50-80 microns.

4) Decomposition of iron carbonyl - $Fe_2(CO)_9$ is decomposed at 200 to 250°C, to give the finest and most expensive of the common types of Fe powder. The average particle size is about 7 microns.

5) Mechanical comminution - Relatively coarse particles are produced by machining.

3.4.3 Experimental work.

The experiments described in the following sections are designed to study the effect of Fe metal on the Pb, or Pb and Cu concentrations in concentrated $ZnCl_2$ solutions. The type of Fe metal used, is varied between three types of powder, (table 3.18), and massive metal. In this way, the effect of each type of Fe metal, on the Pb and Cu concentrations, is studied.

Table 3.18 Type Of Fe Powder Used In Experimental Work.

Fe Powder	% Particle Size (microns)			
	>125	90-125	63-90	<63
"Fe metal powder" (BDH 28600)	46.5	22.5	18.0	13.0
"Reduced by H_2" (BDH 28602)	<1.0	1.0	1.5	>96.5
"Electrolytic" (BDH 28601)	29.0	27.0	24.0	20.0

The experimental conditions are varied in terms of solution temperature, initial Pb concentration, type and weight of Fe used. Also, a parameter, the Fe:Pb mole ratio, (which is derived from the ratio of the number of moles of Fe to the number of moles of Pb initially in solution), is calculated for each experiment, as a means of comparing directly the efficiency of Pb removal by different types of Fe.

In the first series of experiments, the cementation reaction is studied at high temperature, and the Pb concentration is determined after 5 hours. In later experiments, reactions are performed at room temperature, for 1 hour only. Under the less reactive conditions, the results obtained would be more useful when applied to an industrial scale. In a 200ml volume of solution, with magnetic stirring, excellent mixing can be achieved. It is therefore a reasonable assumption, that if the reaction is not complete after 1 hour at room temperature, then the particular reaction would likely to be of little use on a large scale, where hundreds of litres of solution would be involved, and which would likely to be subject to less efficient mixing.

In the 1 hour experiments, the effect of Fe on both the Pb and Cu concentrations is studied. Kinetic experiments, involving a qualitative investigation into the rate of Pb precipitation, is also studied.

All experiments involve 200ml of 35-36% $ZnCl_2$ solution, at pH 1.0 to 1.5, (similar to $ZnCl_2$ process solutions). Mixing of the reaction mixture is kept as constant as possible by using a magnetic stirrer on a fixed setting.

3.4.4 Treatment of hot, concentrated zinc chloride solutions with Fe metal, and the effect on the solution lead concentration.

3.4.4a Effect on Pb precipitation of variations in initial Pb concentration and the weight of "Fe powder" (BDH 28600) used.

200ml volumes of 35% w/w $ZnCl_2$ solution, containing up to 5000mg/ml Pb, as $PbCl_2$, were heated to, and maintained at, 80-85°C, and treated with various weights of "Fe powder", (BDH 28600). The powder was added to the hot solution and the mixture stirred vigorously for 5 hours with a magnetic stirrer. Loss of water, by evaporation, was reduced by placing a cold surface over the opening of the reaction vessel. After the 5 hour period, the mixture was cooled to 20°C, and an aliquot of filtered solution was analysed for Pb concentration by A.A.S. The results of this investigation are shown in table 3.19.

Table 3.19 Effect Of Fe Powder On Pb Concentration In Zinc Chloride Solutions.

Wt. Fe (g)	Fe:Pb (mole ratio)	Pb conc. (mg/l) initial	Pb conc. (mg/l) after 5 hrs
10.0	1529	121.3	1.3
10.0	751	246.9	1.2
10.0	385	481.3	2.4
10.0	247	751.9	3.1
10.0	191	972.3	5.4
10.0	124	1492	4.4

Table 3.19 contd.

10.0	98	1895	4.4
10.0	76	2428	3.0
10.0	68	2742	3.7
10.0	37	4986	2.2
2.0	21	1761	11.3
2.0	21	1765	11.3
2.0	12	2991	4.6
2.0	12	2980	8.9
2.0	9	4078	9.2
2.0	9	3894	10.6
1.0	10	1767	89.0
1.0	10	1766	61.9
1.0	6	2957	59.3
1.0	6	2980	68.4
1.0	8	2188	114.8
1.0	8	2217	40.0

Table 3.19 shows that in all cases, where 10.0g of powder was used, the solution Pb concentration was reduced to <6mg/l, even when the initial concentration was in excess of 1000mg/l. In experiments which used 2.0g of powder, the concentration was reduced from between 1760 and 4080 mg/l to <12mg/l. In each experiment involving 1.0g powder, the concentration was reduced to between 40 and 115mg/l.

3.4.4b Effect on cementation on variations in the type of Fe powder used.

A similar procedure was used to that described in the previous section, with the exception that the type of Fe powder used was varied in order to investigate the effect of this change had on Pb removal. Table 3.20 shows the results obtained.

Table 3.20 Effect Of Type Of Fe Powder On Pb Removal.

Fe metal	Wt. Fe	Fe:Pb	Pb conc. (mg/l)	
	(g)	(mole ratio)	Initial	After 5 hrs
Fe_H	10.0	1855 to 46	100 to 4000	<5
Fe_E	10.0	1855 to 46	100 to 4000	<5
Fe_P	10.0	1855 to 46	100 to 4000	<6
Fe_H	2.0	21.8 to 9.5	1700 to 3900	<12
Fe_E	2.0	21.8 to 9.5	1700 to 3900	<12
Fe_P	2.0	21.8 to 9.5	1700 to 3900	<12
Fe_H	1.0	8.5	2188	271.9
Fe_H	1.0	8.5	2188	153.8
Fe_E	1.0	8.4	2217	458.5
Fe_E	1.0	8.4	2217	201.0
Fe_P	1.0	8.5	2188	114.8
Fe_P	1.0	8.4	2217	40.0
Fe_M	19.3	161.5	2217	954.6
Fe_M	19.3	161.5	2217	426.4

Fe_H = "Fe reduced by H_2" (BDH 28602)

Fe_E = "Electrolytic Fe" (BDH 28601)

Fe_P = "Fe powder" (BDH 28600)

Fe_H = Fe nails (1")

It was found that experiments using 1.0 and 2.0g of powder gave similar results irrespective of the type of powder; the Pb concentration was reduced to <6 and <12mg/l respectively.

Experiments involving 1.0g of powder, reduced the Pb concentration from about 1700mg/l to between 40 and 460mg/l, with the best reduction being achieved by the Fe_P type powder.

Massive Fe was found to be relatively ineffective.

An observation of note occured with experiments involving 1.0 or 2.0g of powder. Soon after the addition of the powder to the hot solution, (<1/2 hour), several spherical pellets formed, the formation of which was seen to be especially rapid when the Fe_H was involved. No powdered metal was seen to be present in the solution after the formation of the pellets, which had a shiny, metallic appearance.

3.4.5 Treatment of concentrated zinc chloride solutions with Fe metal and the effect on the solution lead and copper concentrations.

3.4.5a Kinetic investigation on the effect on the solution lead concentration.

200ml of 36% $ZnCl_2$ solution, at pH 1.2, containing about 350mg/L Pb as $PbCl_2$, was treated with 1.3g Fe_P type powder. The mixture was maintained at 20-23°C, and was stirred vigorously with a magnetic stirrer. The variation in the solution Pb concentration with time was followed by withdrawing aliquots of solution which were then analysed for Pb with A.A.S. The experiment was repeated using Fe_E and Fe_H powders.

The results are given in tables 3.21 to 3.23 and figure 3.8.

Table 3.21 Fe_P Powder

(Fe:Pb = 27.2)

Time(mins)	Pb(mg/l)
0	354.5
29	352.2
56	338.2
93	282.2
117	227.4
177	95.6

Table 3.22 Fe_E Powder

(Fe:Pb = 25.7)

Time(mins)	Pb(mg/l)
0	375.3
36	317.6
59	282.3
80	256.5
97	240.0
180	180.0

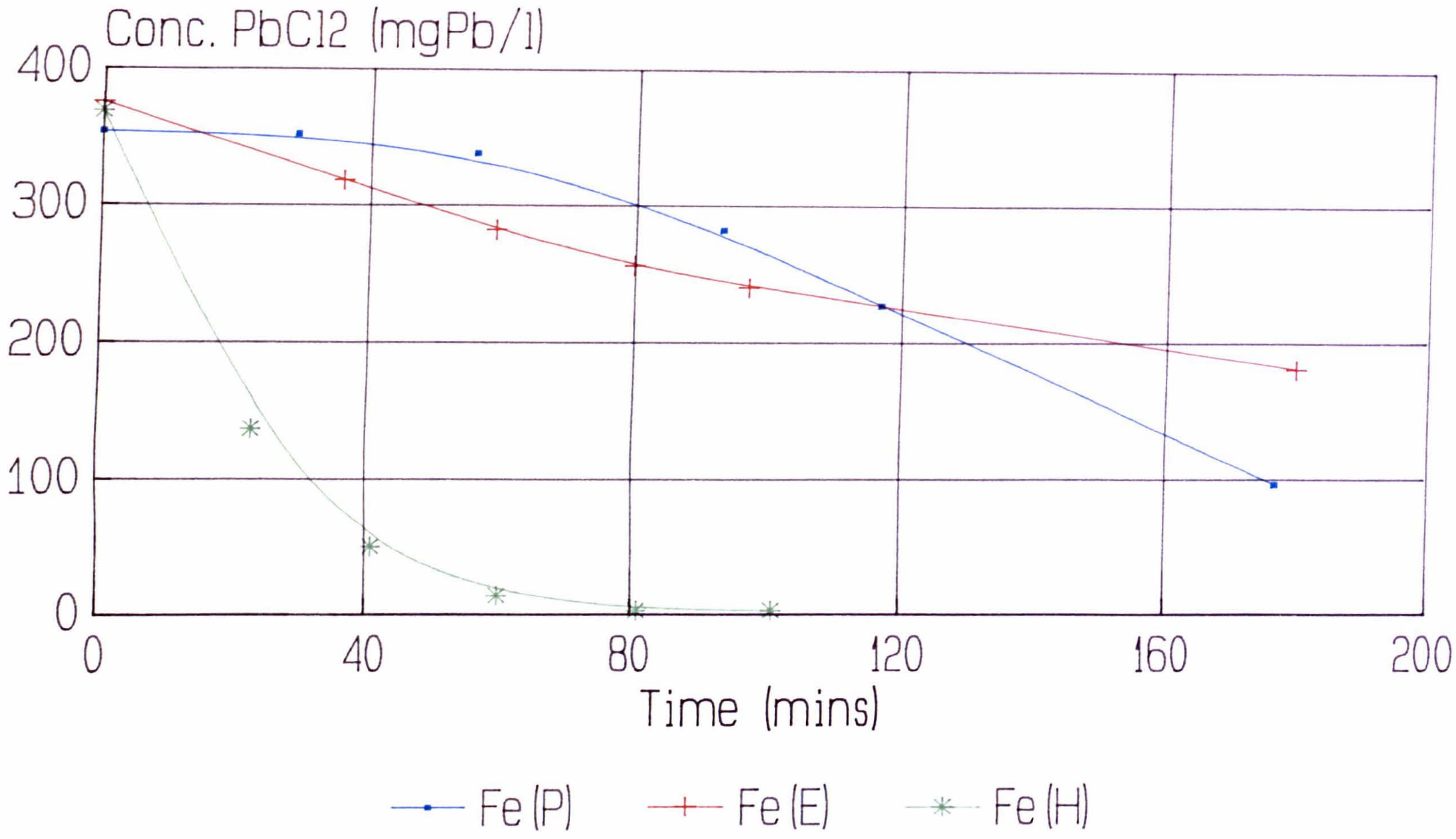

Figure 3.8
Kinetic Study Of Precipitation Of Lead With Iron Metal

Table 3.23 Fe_H Powder

(Fe:Pb = 26.1)

Time(mins)	Pb(mg/l)
0	369.2
23	137.5
41	49.8
60	14.1
81	<5
101	<5

Figure 3.8 shows that Fe_H reduced the Pb concentration to less than 5mg/l in 80 minutes. In contast, the Fe_E and Fe_P powders were considerably less efficient in reducing the Pb concentration. A slow but steady decrease was observed giving values of 180 and 95.6mg/l Pb after 3 hours, respectively.

3.4.5b Effect of varying the weight of Fe_H powder on the solution Pb concentration.

The previous experiment showed that the Fe_H powder has the greatest effect on the Pb concentration under the conditions studied. In the following experiments, the weight of this powder is gradually reduced to determine at which Fe:Pb mole ratio the Pb concentration was no longer significantly reduced.

Samples of Fe_H powder were added to 200ml volumes of 36% $ZnCl_2$

solution containing about 350mg/l Pb as $PbCl_2$. The mixture was stirred vigorously with a magnetic stirrer, and the temperature of the solution was maintained at 20-23°C. After 60 minutes an aliquot of solution was withdrawn and analysed for Pb by A.A.S.

The results are shown in table 3.24 and figure 3.9.

<u>Table 3.24 Effect Of Fe_H On Solution Pb Concentration.</u>

Wt. Fe_H (g)	Fe:Pb (mole ratio)	Pb concentration (mg/l) Initial	After 1 hour
5.4	283.4	353.5	<5
5.4	275.5	363.6	<5
2.6	132.2	364.7	<5
2.6	134.0	359.9	<5
1.3	66.9	360.2	50.6
1.3	68.9	350.2	22.5
0.64	35.1	337.7	310.0
0.64	34.6	342.9	315.0

Very good Pb removal was observed for experiments involving 5.4 and 2.6g powder, (mole ratio 280 and 133 respectively), the concentration being reduced to less than 5mg/l in each case. A further decrease in the weight of powder used, to 1.3g, (mole ratio about 68), was found to decrease the efficiency of Pb removal - a concentration of 20 to 50mg/l was reported after 60 minutes. With 0.64g powder, (mole ratio about 35), little effect was observed.

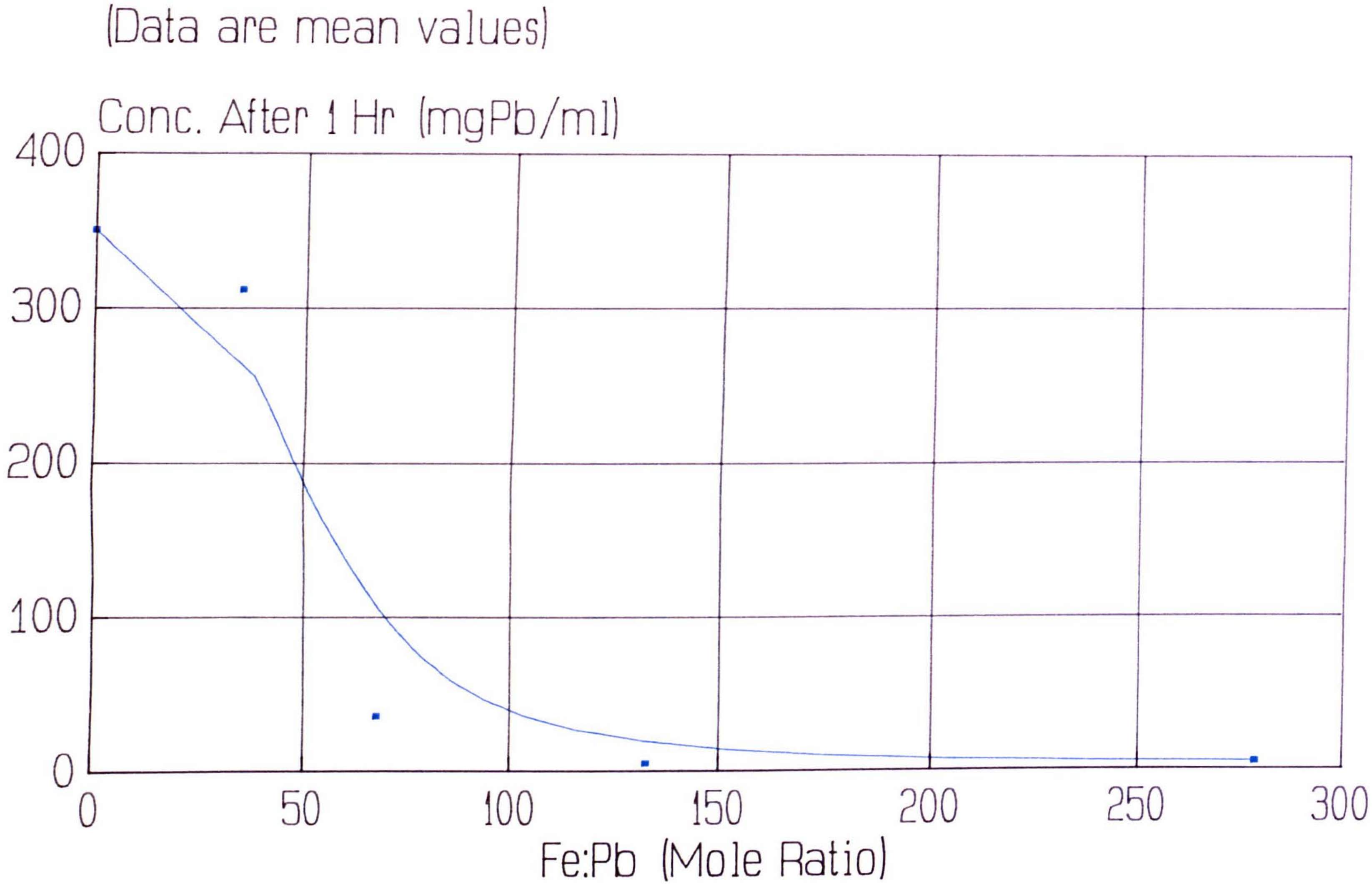

Figure 3.9
Effect Of Wt. Of Fe(H) On The Precipitation Of Pb

3.4.5c <u>Precipitation of Pb and Cu with Fe metal.</u>

The effect of various types of Fe metal on the Pb and Cu concentrations in concentrated $ZnCl_2$ solutions was investigated.

200ml volumes of 36% $ZnCl_2$ solution, at pH between 1.0 and 1.5, containing about 350mg/l Pb and 7.5g/l Cu, as chlorides, were treated with various weights of Fe metal. The solutions were maintained at 20-23°C and were stirred vigorously with a magnetic sirrer. After 1 hour, an aliquot of solution was withdrawn from each experiment and the Pb and Cu concentration analysed by A.A.S.

The results of this investigation are shown in table 3.25. In the table, the value for the Fe;Pb mole ratio was calculated using the weight of Fe remaining after complete precipitation of the Cu in solution by Fe.

Table 3.25 shows that in all cases, the Cu concentration was reduced from 7500mg/l to less than 5mg/l. It was found that this figure was reached in less than 10 minutes, and less than 40 minutes with powder and nails respectively. The cemented Cu was of a powdery nature and did not adhere to the Fe powder.

The effect of Fe metal on the solution Pb concentration was found to decrease in the order $Fe_H \gg Fe_P = Fe_E > Fe_M$ (1" nails), with concentrations of Pb after 1 hour of <5, 115 to 180, approx. 200, and approx. 345mg/l respectively.

Table 3.25 Effect Of Fe On Pb And Cu Concentration.

Fe type	Wt. Fe	Fe:Pb	Pb(mg/l)		Cu(mg/l)	
	(g)	(mole ratio)	Initial	60mins	Initial	60mins
Fe_P	5.4	213.3	354.9	176.1	7500	<2
Fe_P	5.4	194.4	389.4	115.5	7500	<2
Fe_E	5.4	215.8	350.8	201.7	7500	<2
Fe_E	5.4	211.9	357.3	191.0	7500	<2
Fe_H	5.4	214.8	352.5	<5	7500	<2
Fe_H	5.4	208.2	363.6	<5	7500	<2
Fe_M	5.4	219.5	344.9	340.0	7500	<5
Fe_M	5.4	213.3	354.9	350.0	7500	<5

3.4.6 Summary and conclusions.

3.4.6a The removal of lead from 35-36% zinc chloride solutions.

Solutions at 80-85°C.

The results show that if conditions involve a high solution temperature, (80-85°C), and vigorous stirring, which can be assumed to favour the precipitation reaction, then the addition of sufficient Fe metal to the solution will result in a considerable reduction in the lead concentration, and can be achieved irrespective of the type of Fe metal used, of those types studied.

Very low Pb concentrations can be achieved, (<12mg/l over 5 hours), with Fe powders in hot solutions containing up to at least 4000mg/l Pb, as $PbCl_2$, if the Fe:Pb mole ratio, in 200ml of solution, is greater than 9.5.

Solution at 20-23°C.

Fe_H is by far the most effective for Pb removal from solution compared to the two other powders studied. With Fe_E and Fe_P powders, indications are that a reaction time of >3 hours is required to reduce the Pb concentration from about 350mg/l to <100mg/l, with a mole ratio of 25. However, with Fe_H powder, <100mg/l Pb can be attained in about 30 minutes, and <5mg/l Pb in 80 minutes. With a mole ratio of at least 132, <5mg/l can be achieved in less than 60 minutes.

Massive Fe is very ineffective toward Pb precipitation at 20-23°C.

In $ZnCl_2$ solutions which contain both lead and copper chlorides, the precipitation of Pb seems unaffected by the presence of the copper. The precipitation of the Cu occurs relatively rapidly, and leaves excess Fe metal to proceed with the precipitation of Pb from solution.

3.4.6b Reactivity of different types of Fe metal toward Pb precipitation from 36% zinc chloride solutions.

The results clearly show, for solutions at 20-23°C, that weight for weight the Fe_H powder is the most reactive toward Pb precipitation compared to the other two powders and massive Fe. The greater reactivity allows a considerable reduction in the solution Pb concentration to be achieved in a relatively short period of time.

The greater reactivity of the Fe_H powder can be explained simply in terms of the specific surface area, (S.S.A.), of this powder compared to the other two types. Table 3.18, which compares the particle sizes of the three powders, shows that the Fe_H type is the finer, and therefore can be assumed to have the greatest S.S.A.

In a reaction which occurs essentially at the surface of the reagents, such as the cementation reaction, the rate of reaction depends very much on the fineness of the reagents. With this in mind, the four types of Fe metal studied, should have the cementation reactivity in the order $Fe_H >> Fe_E > Fe_P >> Fe_M$. At a solution temperature of 20-23°C, this reactivity series does compare favourably with experimental results.

In $ZnCl_2$ solutions at 80-85°C, the rate of the cementation reaction is considerably faster than at room temperature. On addition of Fe powder to the hot solution, Pb deposits rapidly. Aggitation of the reaction mixture promotes the formation of conglomerates, which contain Fe powder and precipitated Pb. (Soft metals, such as Zn, Sn and Pb, tend to precipitate as spongy metals, which show a tendency to form conglomerates if compacted together.). Further agitation compresses the conglomerates by impaction, ultimately to form hard spherical pellets, of low S.S.A., and the initial reactivity of the Fe powder is lost. With this explanation, it can be seen why the extra reactivity of the Fe_H type powder, compared to the other powders, is no longer an advantage in hot solutions.

In conclusion, it can be said that a lead impurity in a concentrated $ZnCl_2$ solution, can be reduced in concentration by precipitation with Fe metal.

By using powdered Fe, lead can be reduced to very low concentrations, (<12mg/l), rapidly and simply. With reactions at 20-23°C, Fe_H type powder is the most efficient in removing lead from solution compared to Fe_P and Fe_E powders, or massive Fe. At 80-85°C, the 3 powders are equally effective for lead removal.

The precipitation of Cu from concentrated $ZnCl_2$ solutions, to concentrations of <5mg/l, can be achieved effectively and simply with either of the 4 types of Fe studied.

3.4.7 Suggested application of the precipitation of Pb and Cu with Fe metal to the zinc chloride manufacturing process.

The use of Fe metal to reduce the concentrations of lead and copper in concentrated $ZnCl_2$ solutions, as described in the previous sections of this chapter, could be applied to the manufacturing process in two ways:

1) By applying the reaction to the filtered zinc residue leachate prior to the clearing process and omitting a Zn dusting process completely.

2) By applying the precipitation reaction to the zinc residue leachate to remove the copper and the bulk of the lead from solution, but still operating a Zn dusting process, as a final refining step, but on a reduced scale.

In the first proposed application, the aim would be to reduce the concentrations of lead and copper to within the technical specification of the commercial $ZnCl_2$, i.e. <2 and <10ppm respectively. The experimental results obtained on the precipitation of Pb and Cu with Fe metal, do show that the application of this method is possible. However, in practice, the modification of the manufacturing process in the manner described, may be undesirable because it is likely that higher grade reagents, (e.g. ZnO for pH adjustment and the chlorate oxidant), would be required up process, to ensure solution concentrations of copper and lead remain sufficiently low.

The second proposed application, seems more advantageous. The existing $ZnCl_2$ process would remain essentially unaltered, but would require less Zn powder per batch because the bulk of the lead, and almost all of the copper, would be removed from the process solution prior to the Zn dusting stage. A further, possibly more attractive advantage, would be the less stringent control required on the Cu and Pb concentrations in the Zn residue feedstock. The copper and lead in the leachate, would be reduced to acceptable levels early in the process stream, immediately prior to removal of the iron in solution, by the clearing stage. Figure 3.10 illustrates the scheme.

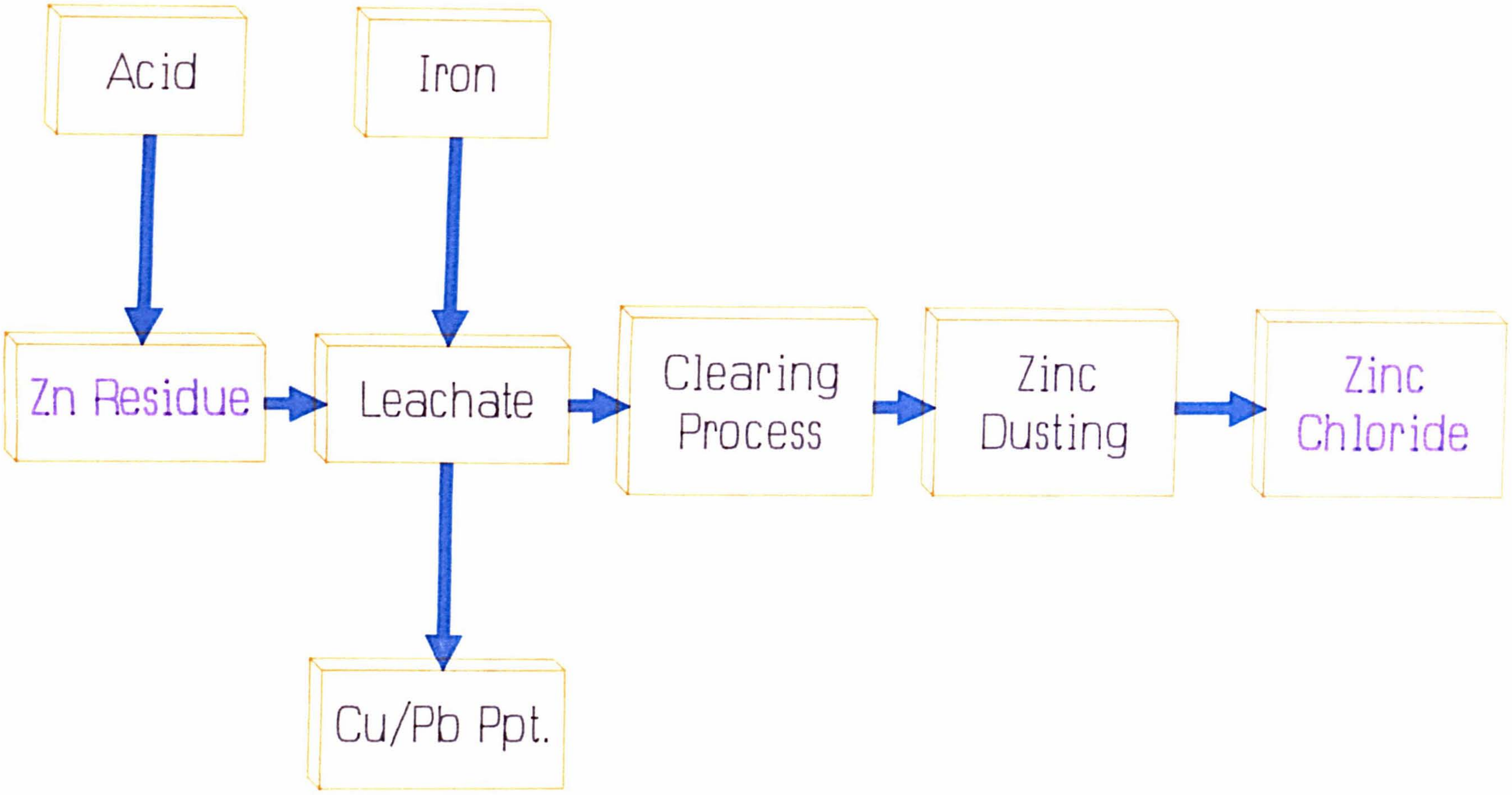

Figure 3.10 Scheme For Modified Zinc Chloride Process.

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CHAPTER 4

AN INVESTIGATION INTO THE METAL EXTRACTIVE PROPERTIES, IN ACID CHLORIDE SOLUTIONS, OF THE WEAKLY BASIC ANION EXCHANGE RESIN POLY-4-VINYL PYRIDINE.

List of Tables and Figures.

4.1 Introduction

Exchange resins can be divided into three distinct groups, viz:

a) Anion exchangers

b) Cation exchangers

c) Resins with metal chelating properties.

The prescence of the weakly basic pyridine nitrogen in poly-4-vinyl pyridine, (PVP), allows the resin to be described technically as an anion exchange resin, but the coordinating ability of the N donor atom also confers chelating type behaviour on the resin.

Previous work on the behaviour of PVP toward metal retention involved investigations into the mechanisms by which the resin removed metal ions from solution. Particular reference should be made to interesting work by Kopylova [29,30], (see section 4.4). Literature references to the practical value of PVP for metal extraction from solution are, however, scarce; the data often being presented only from the standpoint of the metal-resin structural interaction. In view of this, it was regarded that a study on the characterisation of the resin from a practical viewpoint was warranted. Experiments described in this chapter are designed to achieve that aim by investigating the metal loading capabilities of the resin in chloride solutions of varying metal concentration and acidity. A study of concentrated solutions should be particularly important on three counts, viz:

a) Hydrometalurgical leachates, (in which metal recovery and purification are of prime importance), are often concentrated solutions.

2) In the concentrated choride solutions that are often found in metal recovery situations, many metals will be present as anionic

chloride complexes and although the resin is known to show extensive metal chelating ability, no studies of its behaviour in the presence of complexed metal ions have been carried out. The practical use of the resin will depend critically on the relative strengths of the chloro-metallate complexes and the resin-metal chelates.

3) The removal of unwanted metal ions from leach solutions is often necessary, and the ability of PVP to purify solutions by selectively removing metal impurities is important.

These three aspects of PVP are studied in this work. In all experimental work a batch technique was used, and the results were subsequently used to make predictions on the capability of the resin in seperating metals by column chromotography.

The metals studied in the experimental work were selected from those most likely to occur in solutions arising from hydrometalurgical operations.

Prior to the description of the experimental work, this chapter reviews:

a) Anion exchange and anion exchange resins, and includes details on the formation of anionic chlorometallate complexes, and the use of the resins for the retention of metal complexes from solution.

b) Chelation and anion exchange resins with chelating ability.

c) Factors which affect the rate of retention of metal species.

d) Industrial uses of anion exchange resins, including those having metal chelating ability.

e) Vinyl pyridine type resins.

4.2 Anion Exchange And Anion Exchange Resins.

4.2.1 General description.

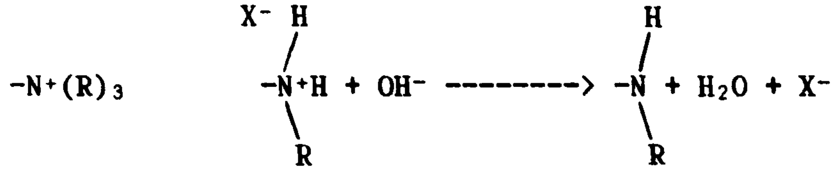
Anion exchange resins, in common with the cation types, are insoluble materials composed of an inert, crosslinked polymer matrix, carrying fixed ionic groups. Associated with these groups are mobile anions or "counter ions", which are capable of exchange with a stoichiometric quantity of anions when in contact with an electrolyte solution. A typical anion exchange process can be written,

$$2RX + SO_4^{2-} \text{------>} R_2SO_4 + 2X^-$$

where R represents the structural unit of the organic matrix, and X the counter ion. An anion exchanger can therefore be described as a cation matrix carrying exchangeable anions.

The exchange process is reversible and usually achieved in solutions containing high concentrations of compounds of the X anion; for example, NaX, KX and HX.

The exchange behaviour of the anion exchange resin , is determined by the fixed ionic groups, while the nature of these groups determines the exchange capacity. The resins can be divided into two groups - those containing weakly basic species such as $-NH_2$, and the strongly basic resins containing quartenary ammonium ions. The base strength of the resins determines their operative pH. Strongly basic resins remain ionised even at high pH values, whereas those containing simple amine groups, are only ionised in acidic enviroments and therefore are not exchange active in alkaline solutions because of the formation of uncharged groups.



$$-N^{+}(R)_3 \qquad \overset{X^{-}\ H}{\underset{R}{-N^{+}H}} + OH^{-} \longrightarrow \overset{H}{\underset{R}{-N}} + H_2O + X^{-}$$

Quartenary ion | Weakly basic secondary amine | Uncharged group

The weakly basic resins were the first type of anion resins to be prepared. Adams and Holmes [1,2] described a patent whereby an exchange resin was manufactured by the condensation of an aromatic amine, (n-phenylenediamine), with formaldehyde. The earlier resins, which were products of condensation polymerisations, tended to be polyfunctional because further reactions with the aldehyde produced secondary and tertiary amine groups. This lack of control over the nature of the condensation products was a major drawback during their preparation, and resulted in the limited use of the earlier resins.

With the development of styrene type addition polymers, a greater degree of control could be used on the extent of crosslinking and functionality induced during manufacture.

Some of the most important anion exchange resins are based on crosslinked styrene polymers [3,4,5,6,7]. Basic groups are produced by chloromethylation of the styrene group, with subsequent treatment with ammonia or alkylamine, or a tertiary alkylamine, to produce anion exchange resins with weakly basic or strongly basic characteristics, respectively. The latter reaction, the "quarternisation" of a chloromethylated resin, is the key reaction in the production of most of the well known, commercial anion exchange resins. Examples include Dowex 1, Amberlite IRA-400 and Duolite A-42, derived from trimethylamine, and Dowex 2, Amberlite IRA-410 and Duolite A-40, derived from dimethylethanolamine. Treatment of the chloromethylated intermediate with a secondary alkylamine, gives a mono-functional weak base resin with tertiary amino groups [8]. By treatment with ammonia and primary alkylamines, polyfunctional, weak base resins are obtained. Examples of resins of this type are Dowex 3, Amberlite IR-45, Nalcite WBR and Duolite A-14.

Anion exchange resins with strong base quartenary phosphoric and tertiary sulphonic groups can also be prepared.

4.2.2 Ion exchange equilibria.

Where equilibrium between an ion exchange resin and exchangeable ions in solution exists, an equilibrium constant K can be defined, such that,

$$K = \frac{[\bar{B}^{n+}][A^{+}]^{n}}{[B^{n+}][\bar{A}^{+}]}$$

for the ion-exchange reaction,

$$n\overline{RA} + B^{n+} \rightleftharpoons \overline{R_nB}^{n+} + nA^{+}$$

where barred species represent those in the solid phase and square bracketed quantities are the equilibrium ionic activities. Where concentrations are used rather than activities, the value K is not a constant, but a purely practical quantity, refered to as the selectivity coefficient $K^{B}{}_{A}$. True equilibrium constants are difficult to obtain due to the lack of reliable data for activity coefficients in the exchanger phase. Studies on ion exchange equilibria are therefore carried out in solutions where reasonable assumptions can be made regarding ion activity coefficients.

Other practical quantities used to define ion exchange equilibria, are the distribution coefficient, K_A [defined as the equilibrium concentration of a given ion in the exchanger, (meq/g), divided by the equilibrium solution concentration, (meq/ml)], and the separation factor, d, [defined as the ratio of the distribution coefficients of both ions in the exchange reaction, $d^{B}{}_{A} = K^{B}{}_{d}/K^{A}{}_{d}$].

Both values are not constants and depend on the experimental conditions under which they are determined, but do provide qualitative comparisons between various ionic species involved in exchange reactions.

4.2.3 Factors affecting the rate of metal retention.

Ion exchange is a diffusion process. Although the actual exchange of ions is probably instantaneous, the rate determining step of the overall exchange reaction, is the interdiffusion of the exchanging ions, either within the exchanger itself, (particle diffusion), or in an adherent liquid "film" which is not affected by agitation of the solution, (film diffusion). Most rate laws concerned with ion exchange, (and sorption processes), therefore involve the use of a quantity, known as the diffusion coefficient, which takes into account the effect of various conditions have on the diffusion process, and hence on the overall kinetics of the ion exchange and sorption reactions. Consistant quantitative predictions on the magnitude of diffusion coefficients are difficult to obtain due to a lack of reliable theory. However a number of resin characteristics and reaction conditions are known to effect the rate of diffusion. These are discussed in a qualitative manner below.

a) Degree of swelling and the mesh width of the resin.

The rate of diffusion increases with an increase in the extent of swelling of the resin, and decreases with the width of the resin matrix [38,39]. The latter effect is particularly important where the mesh width and size of the diffusing species are comparable. One of the most important characteristics of the resin, governing both factors is the degree of crosslinking of the polymer network. Highly crosslinked resins swell only to a relatively limited extent and contain relatively small mesh widths.

b) Size of the ionic species.

The smaller the species, the faster the diffusion in the absence of other effects that interfere. In weakly and moderately crosslinked resins, where the size of the pores allows solvation of the ions to occur, the size of the solvated species determines their mobility. In highly crosslinked resins there is little room for solvation and the size of the non-solvated ions determines the diffusion rate.

c) Valence of the ionic species and the chemical nature of the resin matrix.

Reduction in the mobilities of the diffusing ions can result from electrostatic and specific chemical interactions of the ions with the resin matrix. The extent of this effect can depend on the valence of the diffusing ionic species. Polyvalent ions are, in general, retarded to a greater degree than monovalent ions [38,40,41].

d) Composition of the pore liquid.

The pore liquid, (the solution contained in the interstices of the resin matrix), can be considered to be the medium in which diffusion takes place. Thus its composition, viscosity and degree of ionic solvation, affects the mobilities of the diffusing ions.

e) Temperature.

As in solutions in general, the diffusion coefficient increases with temperature. Normally, the increase in mobility of the diffusing species, is greater in ion exchange than in ordinary aqueous solutions, because with increasing temperature, retarding specific or electrostatic interactions become weaker, the matrix becomes more flexible, and the ions become smaller because solvation is reduced.

The factors outlined above, are particularly important to column operations, because the kinetics of ion exchange has an important effect on the sharpness of elution peaks, and hence on the efficiency of ion separation.

The quantitative theory of ion exchange kinetics is very complex. Even for the simpler problem of ion exchange in batch operations, (compared to the column technique), kinetic theory has only been produced for certain ideal situations. Nevertheless, theories based on drastic simplifications of column kinetics, have been proposed and have often been used to predict the approximate performance of ion exchange columns.

4.3 The Use Of Anion Exchange Resins For Metal Recovery.

4.3.1 Anionic metal - halide complexes.

The existence of anionic metal-halide complexes in solution is fundamental to the ability of true anion exchanging resins to recover metals from solutions of metal halide salts. Reference to the occurance of these complexes are widespread, and fairly well documented. Some species are well known, such as $[FeF_6]^{3-}$, because of the common use of F^- to mask Fe^{3+} when this ion interferes in an analytical procedure. A further example is $[AgCl_2]^-$ which accounts for the relatively high solubility of AgCl in strong hydrochloric acid. The non-existance of anionic halide complexes involving Alkaline and Alkaline Earth metals is also of note.

Information concerning the relative stabilities of different metal halide complexes can be deduced by refering to the appropriate equilibrium constant for the complex forming reaction. Two constants can be refered to, the stepwise or consecutive constant K, and the cumulative or gross constant .

1) Stepwise constant K.

For the reaction,

$$MX_{n-1} + X \rightleftharpoons MX_n$$

where M = metal and X = halide, and concentrations are in mole/l, the constant K_n can be written,

$$K_n = \frac{[MX_n]}{[MX_{n-1}][X]}$$

eg. $Ag^+ + Cl^- \rightleftharpoons AgCl$ $\log K_1 = 3.53$

$AgCl + Cl^- \rightleftharpoons (AgCl_2)^-$ $\log K_2 = 1.81$

2) Gross constant B.

For the reaction,

$$mM + nX \rightleftharpoons M_mX_n$$

$$B_{mn} = \frac{[M_mX_n]}{[M]^m[X]^n}$$

eg. $2Ag^+ + 6I^- \rightleftharpoons (Ag_2I_6)^{4-}$ $\log B_{62} = 30.0$

A considerable amount of data on both constants, K and B, for many inorganic complexes, can be found in the book, "Stability Constants", compiled by the Chemical Society (London), (Special publication No. 13).

Predictions on the relative stabilities of anionic metal halide complexes, based purely on theory, are difficult to make with any accuracy,but workers have in the past, attempted to classify metals into groups depending on their complex halide stabilities. Ahrland and co-workers, noted two classes of metals; type "a", which form complex ions with relative stabilities which decrease in the order $F^- \gg Cl^- > Br^- > I^-$, and type "b", where the order is reversed. Class "a" incorporates the metal ions with inert gas structures, such as Al^{3+} and B^{3+} , and it suggested that complexes are formed primarily by electrostatic attraction with little polarisation of electrons. The metals lying within the triangular region Cu-Os-Bi are classed as "b" type, and characterised by having large ions, of low charge, which are easily polarisable. Multivalent metals on the verge of either class, such as Mo, behave as metals of both types depending on the valency. Higher oxidation states, (eg. Mo^{6+}), exhibits characteristics of class "a". However, lower valences, (eg. Mo^{3+}), where polarisation of the ion can be greater, may be classed as type "b".

The effect of increasing charge on the metal ion does show some predictable behaviour within the two classes. Isoelectronic metal ions of type "a", do show a tendency to form progressively stronger complexes with F^- with increasing metal charge, although stability is limited due to the formation of oxo-complexes, induced by the high charge. For example, Cr^{6+} exists as CrO_4^{2-} in solution. The formation of these oxo-complexes does not, however, exclude their use in ion exchange operations, as the recovery of Cr, as CrO_4^{2-} from wastewater testifies, (see 4.3.4). Isoelectronic ions of type "b", generally form weaker complexes with Cl^-, Br^- and I^- , and stronger complexes with F^-, the higher the metal ion charge.

On descending a group in the periodic table, Stability constants infer that heavier elements tend more toward "b"type behaviour. In this respect, reference can be made to the increased stability of Hg^{2+} and Ta^{3+} for Br^- over F^-, than for Cd^{2+} and Ga^{3+} with the same halide ions. Similarly, the platinum metals, show an increased tendency to complex

Cl^-, Br^- and I^- compared to Fe, in both +2 and +3 oxidation states.

Increasing the solution halide concentration, has two effects on complex formation, Firstly, the charge effects the reaction equilibrium,

$$[M^{x+}] + [X^-] \rightleftharpoons [MX_n]^{(x-n)-}$$

a greater proportion of M^{x+} being involved in complex formation. Secondly, larger concentrations of halide ion, promote the formation of complexes containing increasing number of halide atoms.

4.3.2 Ion exchange of anionic metal complexes.

Although anion exchange resins, by their very nature, are used widely for the exchange of typical anions, (eg. halides, SO_4^{2-}, NO_3^- etc.) between solution and solid phase, this does not necessarily exclude the application of these resins to the retention and recovery of metal species. Many metals are able to form anionic chloride complexes in chloride solutions, the formation of which depends on various factors, (see section 4.3.1). Variation of the relative stabilities of the complexes in solutions of varying hydrochloric acid concentration, enables the separation of metals to be made using anion exchange resins. Indeed, separations of this nature, using column chromotography, are established and valuable procedures. With respect to their behaviour in hydrochloric acid solutions, metals can be divided into three groups, viz:

1) Metals which are not exchanged regardless of acid concentration. (Alkali, Alkaline Earths, Sc^{3+}, Y^{3+}, Al^{3+}, Ni^{2+} and Th^{4+}).

2) Metals showing increasing exchange with increasing acid concentration. (eg. Fe^{3+} and Ru^{3+}).

3) Metals decreasing in exchange activity with increasing acid concentration. (Transition metals, especially second and third row elements).

Many anion exchange studies in hydrochloric acid solutions have been carried out by Kraus, Moore and Nelson [9,10,11], who have written an important series of papers collectively titled "Anion Exchange Studies", which give detailed accounts of the separation of metals in hydrochloric acid solutions, including the separation of ions of Zr and Nb, and of Co and Ni, in HCl/HF and HCl solutions respectively, using the commercial resin, Dowex-1. The ability of anion exchange resins to separate heavy transition metals such as Zr and Nb, by means of their halide complexes, is particularly important because stable aqueous solutions of these elements are only easily achieved by the formation of fluoride and chloride complexes. Indeed, one of the first anion exchange experiments, involved the separation of Hf and Zr, as fluoride complexes, with Amberlite IRA-400. (Huffman and Lilly [12]). Separation of these metals by alternative methods is difficult because of their similar chemical properties and ionic radii.

The use of mixed solvent systems, for separation of anionic metal halide complexes, is often encountered in anion exchange. Mixing an organic solvent, (acetone or ethanol, for example), lowers the dielectric constant and increases electrical forces between ions. Complex ion formation then becomes more favourable. Pioneering work in this field was carried out by Fritz and Pietzyk [13], who investigated the exchange characteristics of resins in solutions with varying hydrochloric acid and organic solvent concentration. The effect of the presence of organic solvents can be considerable. Work by Korkisch [14], showed that in hydrochloric acid solutions, containing Ni, Fe and Co, the normal sequence of retention strengths on a resin, is dramatically altered. In 90% acetone/ 10% water, Fe^{3+} is not retained, whereas Ni^{2+} and Co^{2+} are exchange active.

Separation of metals by exchange of their anionic complexes, is not only confined to species involving halides. Exchange of U^{6+} from solutions of sulphuric acid and nitric acid has been achieved [15]. Separations involving the exchange of oxalate complexes Zr^{4+} and Nb^{5+} [16,17]; platinum metals [18]; Sn^{4+} [19,20]; Sb^{5+} [19,20]; and Te^{4+} [20] have been reported. Mention can also be made of the exchange of hydroxy complexes of Mo^{6+} [21,22],and the platinum metals [18].

4.3.3 Anion exchange resins with metal chelating ability.

A chelating agent is a compound containing donor atoms that can complex with a single metal atom to form a cyclic chelate. The principal atoms in coordination chemistry are N, O and S, each atom having at least one non-bonding electron pair to act as the donor orbital in the complex formation.

Chelate complexes may be either neutral molecules, or positive or negative complex ions, associated with appropriate counter ions to produce electroneutrality.

Just as chelates can be formed with single ligand molecules, incorporation of these ligands onto a cross-linked polymer matrix, produces chelate forming resins.

The distinction between chelate resins and weak base anion exchange resins is often unclear. The capability of many of the latter resins to act as ion exchangers is unquestioned, but in some cases, a clear division of the exchange mechanism into either ion exchange or chelating, is a difficult task, due to the variation of resin property with solution composition [43], and the general vagueness of resin characterisation. For instance, many chelating resins are described technically, as weak base anion exchangers, simply because of the presence of primary, secondary or tertiary amine groups in the polymeric structure.

The chelating reaction, in chelating resins, is a diffusion process, and the general effects on ion exchange kinetics, of the physical characteristics of the resin matrix and the solution composition, described in section 4.2, can equally be applied to the kinetics of both anion exchange and chelation reactions.

The equilibrium constant K, for the reaction involving the coordination of an atom in a functional group, (L), on a resin matrix, with a metal species, (M),

$$n\overline{L} + M \rightleftharpoons \overline{L_nM}$$

(barred quantities represent activities or concentrations in the solid phase)

differs from the constant involved in ion exchange equilibria, in that no resin counter ion is involved,

$$K = \frac{[\overline{L_nM}]}{[\overline{L}]^n[M]}$$

and can be referred to as the overall equilibrium constant, or stability constant, K, it being the product of the individual constants for the stepwise formula reactions.

$$\overline{L} + M \rightleftharpoons \overline{LM} \qquad K = \frac{[\overline{LM}]}{[\overline{L}][M]}$$

$$\overline{L} + \overline{ML} \rightleftharpoons \overline{L_2M} \qquad K = \frac{[\overline{L_2M}]}{[\overline{L}][\overline{ML}]} \qquad \text{etc.}$$

$$K = K_1K_2 \ldots K_n$$

Where more than one metal species exists in solution, a displacement equilibrium exists, similar to a true ion exchange equilibrium, eg.,

$$\overline{ML} + M' \rightleftharpoons \overline{M'L} + M$$

For the reaction shown above, the exchange equilibrium constant K can be written such that,

$$K_m^{m'} = K_{m'}/K_m$$

where $K_{m'}$ and K_m are the overall equilibrium constants for the coordination of the ligand L with M' and M respectively.

Because the donor atoms in the functional groups of the chelating resins, can act as Lewis bases, (good examples being the N atom in resins containing amine and pyridine groups), metal ions have to compete with hydrogen ions for the available donor atoms. The pH of the aqueous system is therefore of considerable importance to the behaviour of a weak base resin, simultaneous equilibria existing, involving both resin protonation and metal chelation,

$$H^+ + \overline{L} \rightleftharpoons \overline{LH^+} \qquad\qquad M^{x+} + n\overline{L} \rightleftharpoons \overline{ML_n}^{x+}$$

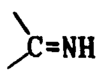
$$K_p = \frac{[\overline{LH^+}]}{[H^+][\overline{L}]} \qquad\qquad K = \frac{[\overline{ML}^{x+}]}{[M^{x+}][\overline{L}]^n}$$

which gives the equation,

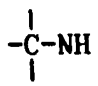
$$[M^{x+}] = [H^+]^2 \times \frac{[\overline{ML}^{x+}]}{[\overline{L}H^+]^2} \times \frac{1}{KK_p{}^2}$$

Therefore an increase in solution acidity results in a decrease in the metal loading of the resin. At an even lower pH the resin is present in a fully protonated form, and is inactive towards chelation, but not necessarily towards ion exchange.

The majority of resins derive their chelating ability from the presence of amine or imine groups in the polymeric structure.



imine



$-\overset{|}{\underset{|}{C}}-NH$

amine

Many studies on the metal loading character of these types of chelating resins have been carried out [43,44,45,46,47,48]. Resins containing the iminodiacetic acid group have been reviewed [49], and the properties of substituted diamine resins, described [50]. Reviews have also been published on commercially available resins, including Dowex A1 [51] and Chelex 100 [17].

Two other important types of chelating resin are those based on vinyl pyridine, (which are dealt with in some detail in section 4.4), and the commercially available Uniselec UR series (Unitika Co., Japan), which are phenolic chelating resins, and which have been used for various purposes [52,53,54,55,56], including the recovery of uranium and nickel from waste water originating from flue gas treatment processes [57], and the removal of iron from acidic zinc plating baths [58]. Reviews on the Uniselec UR series, concerned with their development and applications, have been presented by Arakawa [59] and Uejima [60].

Various reviews on the general subject of chelating resins can be refered to [61,62,63,64], including studies on their applications [65,66], which are usually involved with their use for the removal of heavy metals from waste water [67,68].

4.3.4 Industrial applications.

Since the mid-1970's, the increased need to process poorer quality waters, and the resurgence of the uranium proecessing industry, have been major factors in the growth in the use of ion exchange resins for industrial applications. Improvements, both in resin manufacture and the exchange capabilities of resins, have further enhanced the scope of their use in industry, increasing their advantages, especially from an economic viewpoint, over competing processes such as solvent extraction, crystallisation, dialysis and electrochemical methods. Ion exchange resins are now used widely in industry and several applications can be cited, including:

1) Water treatment - softening; dealkalisation; demineralisation and nitrate removal.

2) Wastewater treatment - removal of radioactive nuclides; heavy metal removal; rinse water recycling.

3) Chemical processing - catalysis; reagent purification; metal extraction and recovery.

4) Sugar separation and purification

5) Small scale uses - pharmaceuticals and reagent/ product analysis.

Some of the more important uses of anion exchange resins in both ion exchange and chelating situations are now described.

4.3.4a Treatment of wastewater.

Anion exchange resins are employed for the treatment of wastewaters, originating from industrial processes, to remove potentially harmful metals, before either the disposal of the water into the enviroment or recycling. The advantages of using resins for these applications are,

a) the resins are non-toxic,

b) subsequent metal recovery is possible, (and certainly desirable where metal values are concerned),

c) the capability of handling waters containing solid matter by batch techniques,

d) resins can be chosen that exhibit metal selectivity, eg between toxic and non-toxic metal, and can improve process efficiency.

The use of anion exchange resins for the recovery of chromate from waste solutions, originating from chromic acid plating or chromate based corrosion inhibiting operations, is particularly widespread. Various resins have been used for this application, including pyridine type weak base exchangers [69] and Amberlite IRA-93 or IRA-400 [70]. In the majority of cases, Cr species in solution are removed as chromate, CrO_4^{2-}, and recovered as a strong chromic solution [71,72,73], Cr concentrations being reduced to less than 2ppm.

Anion exchange resins are similarly employed for general heavy metal removal from wastewaters, especially where the metal is particularly toxic, eg. Hg [74], Cd [75] and As [76]. In some cases, actual recovery of the metal is desirable; for instance where a high metal value is concerned, eg. Pt [77,78].

A general study on the use of anion exchange resins for heavy metal purification of wastewaters, has been carried out by Hirai and Kudo [48], who used phenolic chelating resins to reduce 5-10ppm concentrations of Pb, Cd and Cr to less than 0.01ppm. Many other similar studies can be refered to, including those of Namda and Matsuda [67], Yamada [79] and Ueshima [67].

In the nuclear industry, ion exchange systems are often used for the removal of trace quantities of radioactive nuclides from water intended for release into the enviroment. Generally mixed beds of both anion and cation resins are used. The recovery of neptunium [80] and of americium and curium [81] from plutonium process waters can be cited. The strong base resin, Dowex SBR, has been used for the recovery of technetium from solutions containing a high concentration of fluoride [82]. An interesting study has been carried out by Nabratil and Martella [83], in which various anion exchange resins were investigated, to recover Plutonium from nitric acid waste solutions. Amberlite IRA-938 was reported to give the highest breakthrough capacity, (and the fastest elution rate), for column operations.

4.3.4b Recovery of silver from waste photographic process solutions.

In the photographic industry, considerable silver value is present in the waste solutions originating from the fixing stage of the photographic process. Unreacted silver halides, present in the film coating, are solubilised by complexation with sodium or ammonium thiosulphate, forming complexes of the type, $[Ag(S_2O_3)_2]^{3-}$ and $[Ag(S_2O_3)_3]^{5-}$. Although the silver in these solutions is normally recovered by electrochemical reduction, some use has been made of ion exchange processes on anion exchange resins [84]. Buyers [85], concluded that the use of ion exchange for the recovery of silver from photographic solutions has no advantage over the electrochemical method where non-dilute solutions are concerned (>0.5g/l Ag). But for more dilute solutions, recovery by anion exchange is more favourable, not least from the economic point of view. Liquors originating from the film washing procedure, are one source of such dilute solutions.

The industrial anion exchangers, AV-16-G and AV-17, have been used by Darankov [49], for the extraction of silver , as $[Ag(S_2O_3)_2]^{3-}$, and Koboshi [86], has reported that in solutions containing unusually large concentrations of Br^- and I^-, weak base resins are superior to strong base resins for silver recovery.

4.3.4c Uranium production industry.

The production of uranium from uranium containing minerals is usually achieved via a sulphuric acid leach, following various ore pretreatment steps. In some cases, upgrading of the leach liquor is required, and this can be achieved with strong base anion exchangers [87,88], because uranium has an unusual ability to form anions in sulphate media.

$$UO_2^{2+} + nSO_4^{2-} \rightleftharpoons [UO_2(SO_4)_n]^{2-2n}$$

$$n = 1,2 \text{ or } 3$$

Anion exchange on a resin, R, with a chloride counter ion, occurs via two reactions:

$$4RCl + [UO_2(SO_4)_3]^{4-} \rightleftharpoons R_4[UO_2(SO_4)_3] + 4Cl^-$$

$$2RCl + [UO_2(SO_4)_2]^{2-} \rightleftharpoons R_2[UO_2(SO_4)_2] + 2Cl^-$$

The uranium content of the resin loaded phase, is eluted with NaCl or acid solutions.

In processes using a carbonate leach, complex carbonate anions are formed, and these can also be removed on an exchange resin, by the process:

$$UO_2^{2+} + 3CO_3^{3-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$$

$$4RCl + [UO_2(CO_3)_3]^{4-} \rightleftharpoons R_4[UO_2(CO_3)_3] + 4Cl^-$$

The anion exchange resins that are used for the leach upgrading, are typically Amberlite IRA-400, Dowex 1, Permutit SKB and Deacidite FF. It has been found that conditions can be chosen to enable anion exchange to be very specific for the uranium complexes, with equilibrium being achieved relatively rapidly compared to typical exchange rates. Where the leach liquors exhibit poor settling and filtering characteristics, a modification of the batch type operation, called the resin-in-pulp process, is employed, rather than the usual column technique. In the resin-in-pulp process, the unclarified liquor is contacted with a series of perforated stainless steal baskets, containing the exchange resin. Intimate contact of the resin with the liquor, is achieved by alternately raising and lowering the baskets through the liquor. However, equilibrium is reached more slowly than in the column operations.

After upgrading of the leach liquor, the uranium in solution is precipitated with sodium or ammonium hydroxides. The precipitates normally contain about 80% U_3O_8.

4.3.4d Uranium isotope separation.

Most nuclear power stations employ uranium fuel which has been enriched with the 235 isotope. Fuel enrichment is normally achieved using the gaseous diffusion process, whereby gaseous UF_6, is allowed to diffuse through diffusion barriers, the different rates of diffusion of the 235 and 238 isotopes enables isotope separation to be effected.

During the 1970's, workers at the Asahi Chemical Industry Co. Ltd., developed and patented, a process for the separation of the uranium isotopes on anion exchange resins [89,90,91,92,93]. A solution containing U^{6+} complex ions, is passed through an anion exchange column, where the complexes are absorbed. A reducing agent is then used to elute the uranium species and reduce the uranium to U^{4+}. The resulting eluate is percolated through a second anion exchange column, containing an oxidising agent, where the U^{4+} complex ions are oxidised to U^{6+} and absorbed by the exchange resin. The enrichment factor over a limited number of redox cycles, falls short of that required by most nuclear industries, but economic factors make the use of this method for isotope enrichment desirable on an industrial scale. Various resins for this application are described by the authors, including those obtained from the chloromethylation and amination of cross-linked polymers, prepared from the addition polymerisation of styrene, vinyl toluene or ethylvinylbenzene with divinylbenzene. The functional groups are tertiary amines.

4.3.4e Metal extraction.

In the extraction of metals from ores, tailings etc., where the leach solutions can contain large quantities of contaminants and relatively small concentrations of the desired metal, especially where precious metals are concerned, ion exchange resins can be employed to selectively isolate and concentrate the desired metal. A good example of this type of extractive technique, involving uranium, has already been discussed, (see 4.3.4c), but further, perhaps less well known examples, can be refered to. The extraction of gold from ores and process tailings is often achieved with a cyanide leach. By aeration of the leach liquor, the gold is dissolved by the formation of $[Au(CN)_2]^-$ complex ions. The gold is ultimately recovered by precipitation with zinc dust or aluminium metal. Recently, anion exchange resins have been used to advantage, by incorporating them insitu with the cyanide leach liquor [94,95,96]. In this method, the gold complexes formed during cyanidation, are rapidly absorbed by the resin. At equilibrium, separation of the resin from the undissolved solids is achieved with an appropriate sieve, or in some cases, the resin-in-pulp process, (see 4.3.4c), has been used. Introduction of anion exchange resins into gold extraction processes, has been reported to increase the rate of leaching and eliminate several process steps, such as filtration and clarification of the leach liquor. Increased gold recovery has also been reported [96].

Reference can also be made to the improved recovery of selenium and tellurium [97], and of beryllium [98], using anion exchange resins in similar extractive processes to those for gold.

A general review on the use of ion exchange resins in hydrometallurgy, in which the commercial exchangers available on an industrial scale, and the results of their applications, are detailed, have been presented by Samborskii and Vakulenko [99].

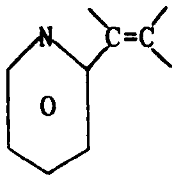
4.3.4f Upgrading of water purity.

The purification of water for the use in non-sterile pharmaceutical products using Ambergard XE-352 resin, has been described by Scruton [100]. Kovac [101] has reviewed the use of anion exchange resins for the preparation of high quality water, free of metal contaminants, for the milk industry.

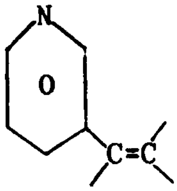
In conclusion, it can be said that anion exchange resins have important, but at the same time, perhaps limited roles to play in industrial processes. Limited in the sense that the application is generally restricted where a relatively low quantity of the metal is present. Larger quantities require progressively higher numbers of exchange/elution cycles, which is simply not practical or economically viable on an industrial scale. But in solutions where high concentrations are present, compared to the desired metal, for example in precious metal leach liquors, the flexibility of exchange resins, with respect to metal selectivity, can be fully exploited, and used to great advantage over other metal recovery techniques.

4.4 Vinyl Pyridine Type Anion Exchange Resins.

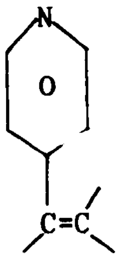
Polyvinyl-pyridine type anion exchangers are derived from the vinyl-pyridine monomer.



2-vinyl pyridine



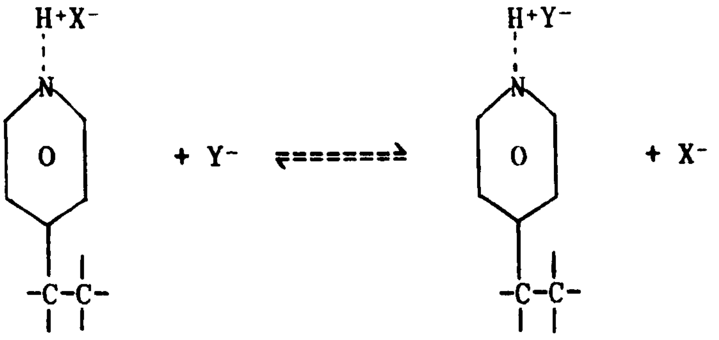
3-vinyl pyridine



4-vinyl pyridine

Polymerisation occurs via the vinyl group. In practice, the polymers are usually cross-linked with 5-10% divinylbenzene, (DVB), to produce insoluble resins with resonable resistance to thermal degradation, although the use of variuos other crosslinking agents is not uncommon. Included in this group are divinylacetylene and vinylcyclohexane [23,24,25]. An anion exchanger, produced from the copolymerisation of vinylpyridine and vinylbenzylchloride, is reported to possess high thermal stability in acid and alkaline solutions [26], thermal stability being attributed to the presence of the aromatic and pyridine rings in the structure. Gorodnev [27], in a detailed DTA study of the thermal stability of vinylpyridine exchangers, reported that the physiochemical characteristics of the resins, remain unchanged up to 160°C. Resins with increased mechanical strength and heat resistance can be produced by conducting the copolymerisation of vinylpyridine and DVB, in the presence of vinylcarbonate [28].

Vinylpyridines derive their anion exchange activity from the protonation of the pyridine nitrogen. Thus they can be refered to as weak base anion exchangers



Although the resin could remove anionic metal species from solution by this mechanism, an alternative process involving the complexing ability of the N-donor atoms of the pyridine rings, is possible. A considerable proportion of their retentive power has, in fact, been attributed to the coordination of metals directly to the nitrogen of the pyridine ring. In a detailed investigation into the methods of sorption of metals by ion exchange resins, with reference to vinylpyridines in particular, Kopylova [29,30], studied the shift and intensities of absorption bands in the infra-red spectrum attributed to different N-metal vibrations. It was shown that the initial infra-red spectrum of poly-4-vinylpyridine, comtained peaks at 1598 and 1630/cm, corresponding to non-protonated and protonated pyridine nitrogen, respectively. After the resin had come into contact with various transition metals however, the 1598/cm band was shifted by up to 18/cm, the absolute value depending upon the metal involved. The intensity of the 1630/cm band was diminished. The shift was found to corrolate with the energy of the N-metal bond, which decreases in the order Cu>Ni>Cd>Co>Zn.

That the degree of protonation or hydration of the pyridine nitrogen is an important factor in the determination of retention characteristics of vinylpyridine resins, was recognised by Saldadze [31].

Various mechanistic and kinetic studies on the sorption of metals by vinylpyridine exchangers have been published. The sorption of Bi on resins of various structure, was investigated by Nad'ol, Kuseleva and Kopievher [32]. A polarographic study on the kinetics of anion exchange of chloride complexes of Zn and Cd, was described by Asambadze [33]. Results achieved, suggested the inner diffuse character of the resin, is an important factor in the retentive process. The sorption of tungsten by 2-methyl-5-vinylpyridine, and quantitative extraction of Mo^{6+} and W^{6+}, by polyfunctional, amino-substituted vinylpyridine resins, have also been investigated [34]. Other general studies, include those of Paslikov [35], and Saldadze [31].

References to patents on the industrial applications of vinylpyridine resins are sparse, but two examples are:

a) The use of poly-4-vinylpyridine, DVB cross-linked resin for the recovery of Cr from dye industry waste liquor, originating from a mordant dyeing process [36].

b) The development of a process to recover pure uranium from sulphuric acid solutions, containing approximately 550ppm U, with a 9% DVB cross-linked resin, in which 99% recovery, has been reported [37].

4.5 Poly-4-vinylpyridine Metal Extraction Experiments.

4.5.1 Preparation of the resin for the experimental work.

The resin used for the experimental work, was in 10 mesh bead form, cross-linked with 6% DVB.

4.5.1a Resin pretreatment.

The pretreatment stage, involved completely stripping the resin of any metal loaded phase, using strong hydrochloric acid

$$\text{metal loaded resin} \xrightarrow{HCl} \begin{array}{l}\text{metal free,}\\ \text{protonated resin}\end{array} + \text{metal chloride}$$

4.5.1b Resin activation.

Pretreatment of the resin using acid, was followed by an activation stage, in which the resin was prepared in the free base form, using strong ammonium hydroxide.

$$\begin{array}{l}\text{metal free,}\\ \text{protonated resin}\end{array} \xrightarrow{NH_4OH} \begin{array}{c}\text{unprotonated}\\ \text{resin}\end{array} + NH_4Cl + H_2O$$

Use of the resin in the free base form in subsequent experimental work, allowed the effects on metal loading, of varying degrees of resin protonation, resulting from contact of the activated resin with varying concentrations of hydrochloric acid, to be studied. (Section 4.5.4).

In each case, 2M solutions of HCl and NH_4OH, were used, using volumes of solution approximately twice the resin volume. The solutions were stirred with the resin for 15 minutes with HCl, and 60 minutes with NH_4OH. Slow stirring speeds were used to avoid excessive attrition of the resin beads. After each stage, the resin was filtered under suction, and washed several times with distilled water. Special attention was paid to efficient washing of the resin, to remove all traces of ammonia solution.

If the resin was to be stirred after activation, care was taken to prevent drying out, by keeping it in a closed, moist atmosphere.

The choice of using two stages for resin activation, rather than ammonia solution alone, was found to be desirable on two counts. Firstly, the use of an acid pretreatment stage, avoided problems associated with metal hydrolysis in alkaline solution, and secondly, the stripping reaction using acid, was found to be very rapid, the reaction going to completion almost immediately on addition of the acid. the rapid reaction with HCl could be seen by the rapid colour change of the resin. (Most metals, when retained, were found to distinctly colour the resin. Copper, for example, showed an intense blue colouration, whereas the unloaded form of the resin, was pale yellow).

4.5.2 General experimental procedure

The experiments described in section 4.5, are based on the determination of the quantity of metal retained by a known weight of resin, when equilibrium conditions are reached between the resin and the metal in solution. In the cases where solution purifications are involved, the experiments decribed are based on the determination of the residual metal concentration.

Each experiment used a sample solution of either 50 or 100ml, (containing a known quantity of standardised hydrochloric acid, and an A.R. grade metal chloride), which was equilibrated with 8-10g of moist resin, activated in the free base form, (see 4.5.1). All experiments were conducted at 20-22°C, and the solutions were well stirred during the reaction period. The length of time needed to reach equilibrium was determined by measuring the solution concentration at various time intervals. Under the experimental conditions described, equilibrium was reached in 30-40 minutes, but in practice, one hour was allowed before each experiment was terminated.

4.5.2a Determination of metal loading.

To determine the weight of metal retained at equilibrium, an indirect method, (subtracting the quantity of metal remaining at equilibrium from that present initially), was used for the preliminary experimental work, but, because of various impracticalities, was soon abadoned in favour of a direct method, (stripping the metal from the resin using a suitable reagent and determining the quantity of metal in the resultant solution).

When equilibrium had been reached, the resin was filtered, and the pH of the filtrate measured. The resin was then washed 3 times with distilled water to remove residues of sample solution. The metal content of the resin was stripped using two 25ml portions of 2M HCl, slurrying the acid/resin mixture thoroughly before filtration. Finally, the resin was again washed with distilled water, (two 20ml volumes), before the solution comprising the acid stripped phase and the final wash filtrates, was analysed for metal content by A.A.S.

4.5.2b Determination of residual metal concentration.

At equilibrium, the resin/solution mixture was filtered, and the pH of the filtrate measured. The filtrate was then analysed for metal content by A.A.S.

4.5.3 Presentation of results.

Results of the experimental work are presented in tabular form, and, where possible, illustrated with graphs. Loading curves are produced by plotting % loading against initial pH of the solution, or the initial metal concentration.

$$\% \text{ loading} = (W_M/W_R) \times 100$$

W_M = wt. metal stripped from resin, and W_R = calculated dry wt. of resin used. The percentage dry weight of each new batch of activated resin, was generally in the range 47 to 53%.

Each loading curve is presented with a specific weight of resin to volume of solution ratio, W_R/V, and to enable direct comparisons to be drawn between loading curves of different metals, the W_R/V parameter was held reasonably constant and generenly in the range 0.045 to 0.050g/ml.

4.5.4 Effect of solution pH on metal loading of the resin.

The effect of the initial solution pH on the loading capability of the resin, was investigated using the procedure decribed in 4.5.2

Loading values were determined for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Ca^{2+} and K^{+}, in solutions varying in pH from 0.28 to a maximum of 4.7 and with metal initial metal concentrations of 0.5 and 10.0g/l. The results, except for Fe^{3+}, Ca^{2+} and K^{+}, are given in tables 4.1 to 4.5, and shown graphically in figures 4.1 and 4.2. For Fe^{3+}, Ca^{2+} and K^{+}, loadings of <0.01% were observed and therefore no further data are presented.

A common shape for the loading curve is observed for all elements. The data infers that high acidity prevents metal retention, and % loading does rise sharply as the pH becomes less acidic, reaching a maximum loading between pH 0.75 and 1.25, before falling steadily to lower loading values as the pH approaches neutral. Higher loading values are achieved for Cu^{2+} relative to the other ions studied.

At least a ten-fold increase in the maximum loading figures are observed when the initial metal concentration is increased from 0.5 to 10.0g/l.

Table 4.1 Copper Loading With pH.

0.5g/l Cu; W_R/V = 0.065g/ml (upper table)

10.0g/l Cu; W_R/V = 0.047g/ml (lower table)

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
11.80	6.43	0.28	1.14	<2	<0.03
11.60	6.32	0.50	2.50	30	0.47
11.90	6.00	0.67	3.18	34	0.57
12.10	6.59	0.97	3.59	34	0.51
13.40	7.30	1.28	4.00	30	0.42
12.21	6.65	1.96	4.23	15	0.23
12.20	6.65	4.70	5.60	14	0.21
9.21	4.69	0.28	1.18	21	0.45
9.11	4.64	0.50	2.30	185	3.99
9.22	4.69	0.67	2.99	427	9.10
9.21	4.69	0.97	3.52	441	9.40
9.53	4.85	1.28	4.15	329	6.78
9.44	4.80	3.70	$Cu(OH)_2$ precipitation.		

Table 4.2 Nickel Loading With pH.

0.5g/l Ni; W_R/V = 0.054g/ml (upper table)

10.0g/l Ni; W_R/V = 0.050g/ml (lower table)

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
10.80	5.53	0.28	1.15	<1	<0.01
11.01	5.64	0.50	2.54	3	0.05
10.30	5.17	0.68	3.21	6	0.12
10.52	5.39	0.97	3.68	13	0.24
10.29	5.27	1.28	4.21	13	0.25
11.20	5.73	1.96	5.65	7	0.11
9.20	4.84	0.28	1.17	<1	<0.01
9.31	4.90	0.50	2.50	42	0.86
9.50	5.00	0.68	3.19	137	2.73
9.32	4.90	0.97	3.84	141	2.88
10.00	5.26	1.28	4.25	113	2.15
9.22	4.84	1.96	4.39	60	1.24
9.21	4.84	4.60	5.71	<1	<0.01

Table 4.3 Cobalt Loading With pH.

0.5g/l Co; W_R/V = 0.052g/ml (upper table)

10.0g/l Co; W_R/V = 0.049g/ml (lower table)

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
10.30	5.32	0.28	1.17	<1	<0.01
10.30	5.32	0.50	2.63	<1	<0.01
10.82	5.65	0.68	3.31	1	0.02
10.11	5.23	0.97	3.82	2	0.04
10.10	5.22	1.28	4.11	3	0.06
9.40	4.86	1.96	5.80	1	0.02
9.67	4.93	0.28	1.18	<1	<0.01
9.81	5.00	0.50	2.51	31	0.63
9.53	4.86	0.68	3.12	63	1.29
9.80	5.00	0.97	3.87	103	2.07
9.79	5.00	1.28	4.10	95	1.91
9.65	4.92	1.96	5.20	23	0.46

Table 4.4 Zinc Loading With pH.

0.5g/l Zn; W_R/V = 0.049g/ml (upper table).

10.0g/l Zn; W_R/V = 0.046g/ml (lower table).

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
9.81	5.01	0.28	1.18	<1	<0.01
9.99	5.10	0.50	2.59	1	0.02
9.80	5.01	0.68	3.31	2	0.05
9.40	4.80	0.97	3.90	5	0.11
9.61	4.91	1.28	4.19	5	0.10
9.72	4.97	1.96	4.75	4	0.08

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
8.40	4.23	0.28	1.17	18	0.43
9.30	4.69	0.50	2.51	37	0.79
9.61	4.85	0.68	3.16	85	1.76
9.00	4.54	0.97	3.79	111	2.44
9.33	4.71	1.28	4.15	80	1.70
9.62	4.86	3.30	5.31	15	0.31

Table 4.5 Cadmium Loading With pH.

0.5g/l Cd; W_R/V = 0.049g/ml (upper table).

10.0g/l Cd; W_R/V = 0.049g/ml (lower table).

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
9.81	4.92	0.28	1.17	<1	<0.01
9.70	4.87	0.50	2.63	1	0.02
9.72	4.88	0.67	3.30	2	0.04
9.89	4.96	0.97	3.85	2	0.05
9.68	4.86	1.28	4.19	2	0.05
9.75	4.89	3.15	4.81	1	0.03
9.59	4.89	0.28	1.19	2	0.05
9.70	4.95	0.50	2.48	33	0.66
9.68	4.94	0.67	3.21	47	0.95
9.58	4.89	0.97	3.84	58	1.18
9.61	4.90	1.28	4.18	59	1.20
9.61	4.90	3.05	5.59	46	0.95

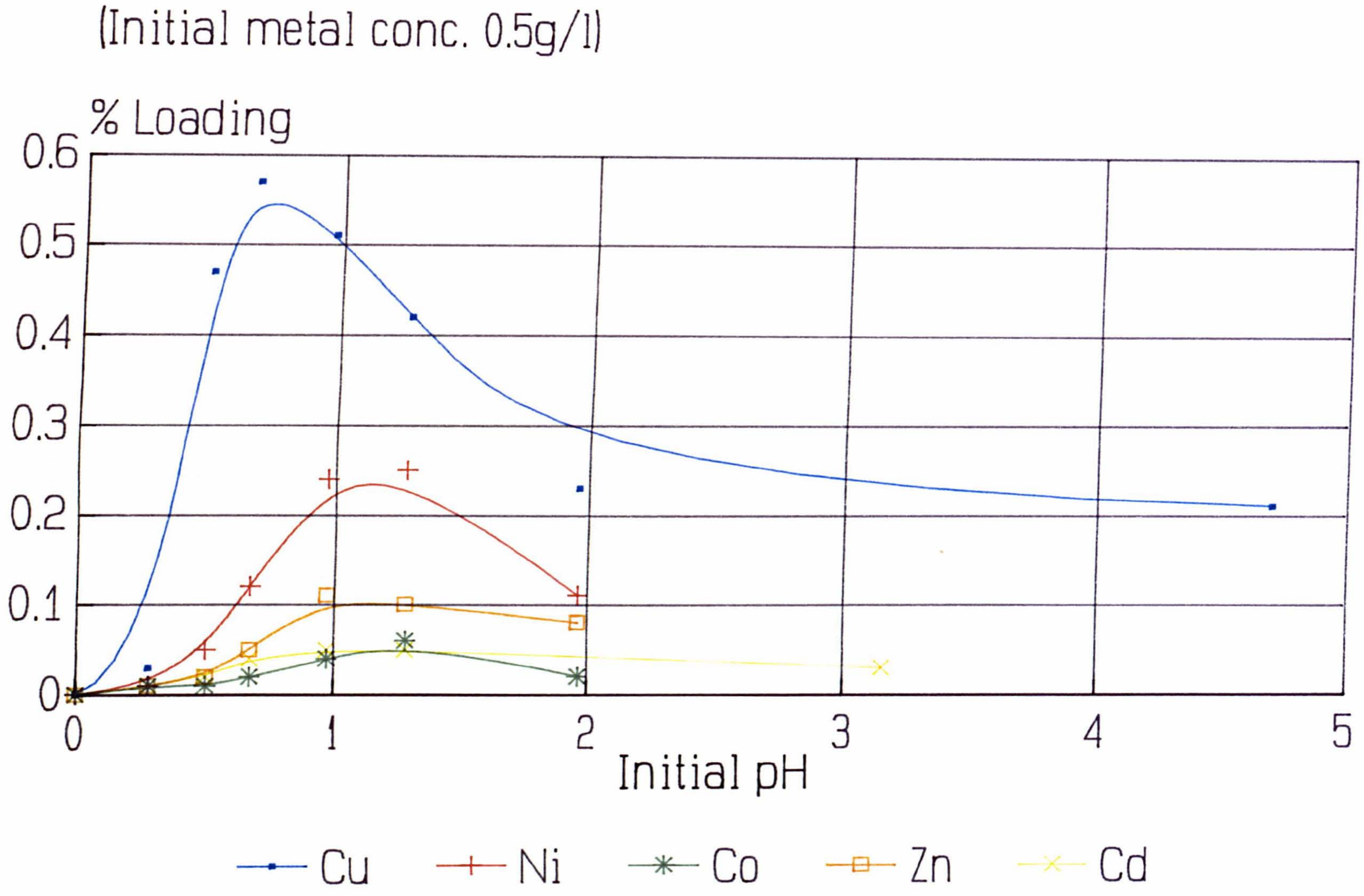


Figure 4.1
Effect Of Initial pH On Loading

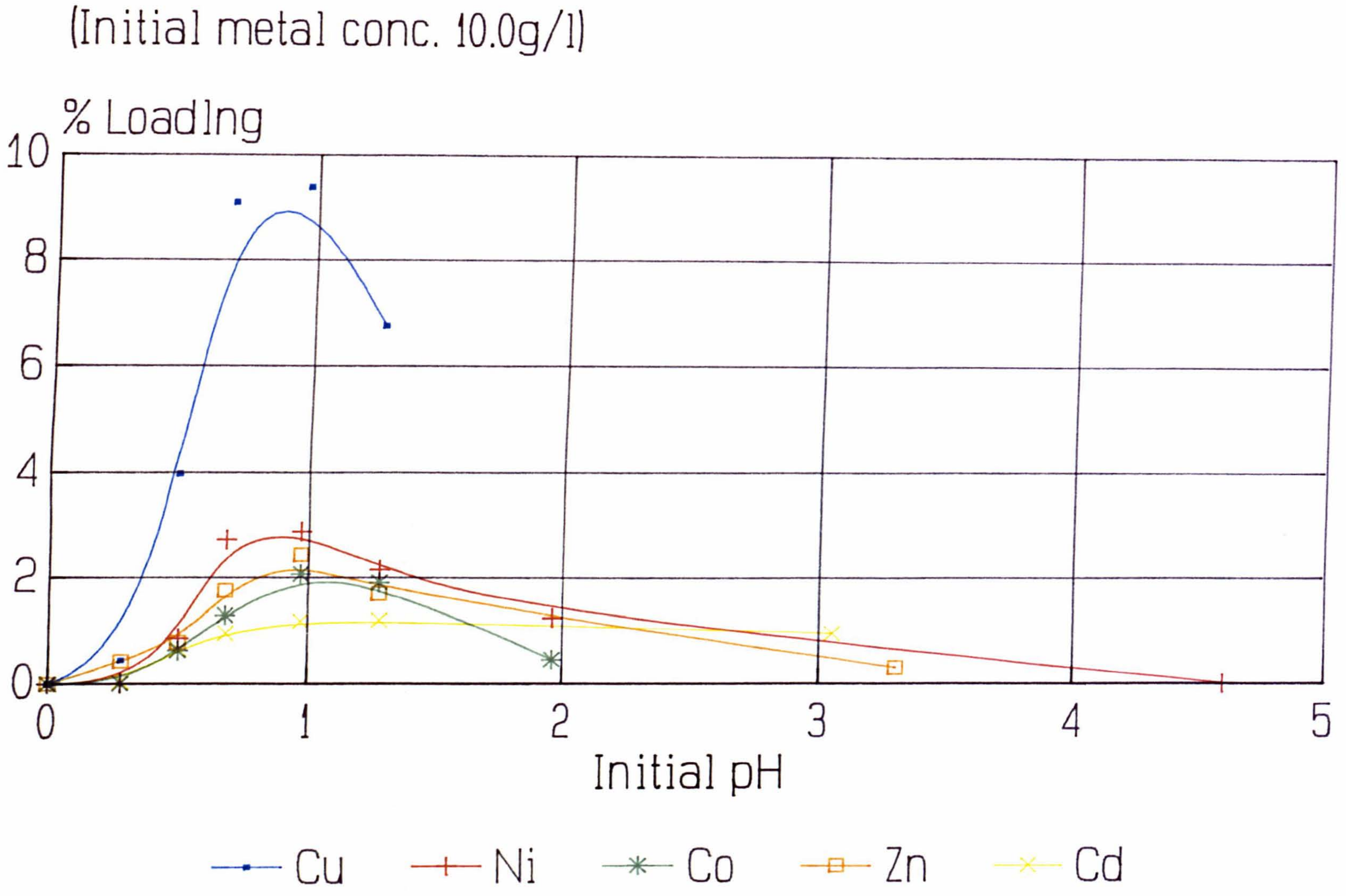


Figure 4.2
Effect Of Initial pH On Loading

4.5.5 Effect of initial metal concentration on loading.

In view of the considerable difference observed between maximum loading values obtained in solutions containing initially 0.5 and 10.0g/l metal, (see 4.5.4), the effect of the initial metal concentration on the metal loading of the resin, was investigated in more detail, at a pH corresponding to the approximate value at which maximum loading occurs.

Loading values were obtained for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}, at pH 0.68, using the procedure described in 4.5.2, for solutions varying in initial metal concentration from 1.0 to 20.0g/l. Results are given in tables 4.6 to 4.8, and in figure 4.3.

Reference to the graph in figure 4.3, reveals a steady increase in the loading capacity of the resin, with increasing initial metal concentration. However, the loading capacity reaches an apparent maximum, when the initial concentration is in excess of 20g/l metal. The resin achieves greater loading values for Cu^{2+}, relative to Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}.

Table 4.6 Effect Of Metal Concentration On Loading.

Cu; W_R/V = 0.050g/ml (upper table).

Ni; W_R/V = 0.048g/ml (middle table).

Cd; W_R/V = 0.051g/ml (lower table).

Resin wt. (g)	Cal. dry wt. (g)	Initial metal conc. (g/l)	Wt. loaded metal(mg)	Loading %
9.41	4.76	1.0	59	1.24
10.11	5.12	2.5	163	3.20
9.60	4.86	5.0	276	5.68
10.00	5.06	9.0	455	8.99
10.00	5.06	20.0	541	10.69
9.40	4.93	1.0	15	0.30
9.22	4.82	2.5	48	1.00
9.00	4.72	5.0	94	2.00
9.09	4.75	9.0	124	2.60
9.21	4.82	20.0	145	3.01
9.40	5.04	1.0	<1	<0.05
9.40	5.04	2.5	9	0.18
9.61	5.15	5.0	21	0.41
10.00	5.36	9.0	55	1.03
9.43	5.05	20.0	84	1.66

Table 4.7 Effect Of Metal Concentration On Loading.

Co; W_R/V = 0.045g/ml (upper table)

Zn; W_R/V = 0.048g/ml (lower table)

Resin wt. (g)	Cal. dry wt. (g)	Initial metal conc. (g/l)	Wt. loaded metal(mg)	Loading %
8.81	4.40	1.0	3	0.07
9.00	4.50	2.5	7	0.15
8.72	4.36	5.0	17	0.40
9.70	4.85	9.0	59	1.22
8.90	4.45	20.0	80	1.80
9.50	4.67	1.0	5	0.11
10.21	5.03	2.5	26	0.52
9.62	4.74	5.0	58	1.22
9.50	4.67	9.0	69	1.48
9.51	4.67	20.0	127	2.71

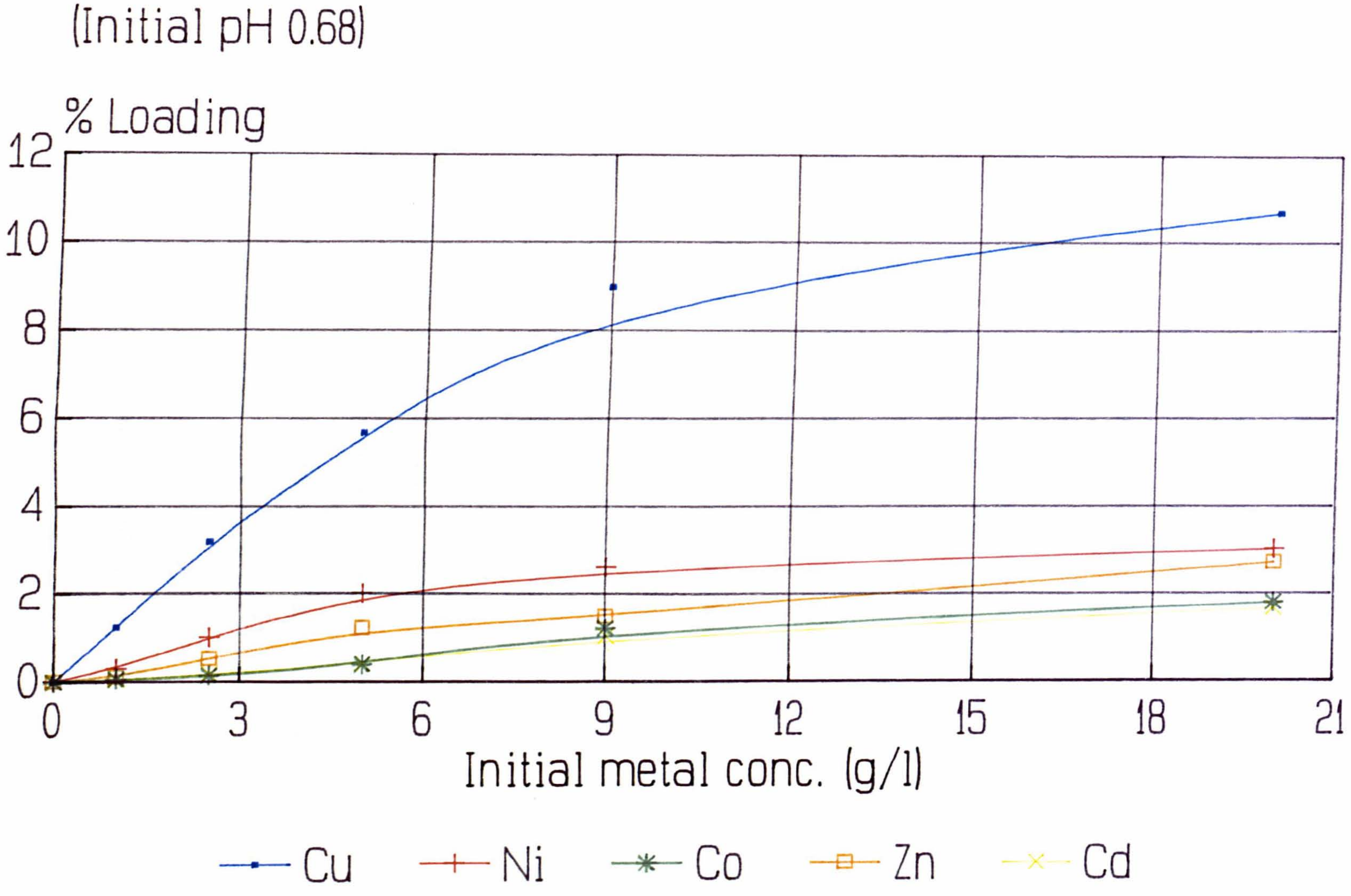


Figure 4.3
Effect Of Metal Conc. On Loading

4.5.6 Loading characteristics of the resin in solutions of high chloride concentration.

Many metals, particularly the transition metals, are able to form anionic chloride complexes, so enabling them to participate in anion exchange reactions with suitable counter ions on exchange resins. (See 4.3.1 and 4.3.2). Poly-4-vinyl pyridine can, in theory, act as a weak base anion exchange resin. (See 4.4). The possibility of metal retention by PVP, by anion exchange of metal chloride complexes, has therefore to be considered. The effect of a high chloride:metal ratio, (where an excess of chloride would promote the formation of metal chloride complexes), on the metal loading of the resin was investigated.

Loading values where determined for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Fe^{3+} by following the procedure given in 4.5.2, in solutions varying in pH from 0.28 to approximately 4, and containing an initial metal concentration of 0.5g/l with a concentration of 40g/l KCl.

A preliminary experiment involving Cu^{2+}, an ion known to form complex halides, showed an enhancement for loading values in solutions up to a maximum of approximately 20g/l KCl, with no further increase in loading observed above this concentration.

Results are given in tables 4.8 to 4.10, and shown graphically in figures 4.4 and 4.5.

Reference to the data shows that the presence of the KCl produces greater loading values in all cases, with marked increases in loading observed particularly for Cu^{2+} and Ni^{2+}. No data data presented for Fe^{3+} because of the precipitation of the hydroxide during the experiments.

Table 4.8 Effect Of High Chloride Concentration On Loading.

Cu; W_R/V = 0.045g/ml (upper table).

Ni; W_R/V = 0.046g/ml (lower table).

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
8.21	4.46	0.28	1.24	<1	<0.01
8.70	4.72	0.50	3.45	37	0.78
8.30	4.51	0.68	4.10	42	0.93
8.50	4.61	1.28	4.75	43	0.93
8.23	4.47	1.97	4.98	40	0.89
8.40	4.08	3.50	5.39	44	1.08
9.26	4.63	0.28	1.24	<1	<0.01
9.21	4.60	0.50	3.62	17	0.36
9.25	4.62	0.68	4.28	30	0.65
9.17	4.58	0.97	4.64	37	0.81
9.32	4.66	1.28	4.94	36	0.97
9.20	4.60	3.15	6.70	<1	<0.02

Table 4.9 Effect Of High Chloride Concentration On Loading.

Co; W_R/V = 0.044g/ml (upper table).

Zn; W_R/V = 0.046g/ml (lower table).

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
9.31	4.37	0.28	1.23	<1	<0.01
9.39	4.40	0.50	3.51	9	0.02
9.48	4.45	0.68	4.39	16	0.36
9.28	4.35	0.97	4.74	27	0.62
9.29	4.36	1.28	4.91	29	0.66
9.13	4.28	3.48	7.0	<1	<0.01
9.58	4.66	0.28	1.24	<1	<0.01
9.41	4.58	0.50	3.40	4	0.09
9.40	4.57	0.68	4.32	7	0.16
9.14	4.44	0.97	4.64	11	0.25
9.49	4.61	1.28	4.88	11	0.24
10.28	5.00	3.50	6.81	4	0.07

Table 4.10 Effect Of High Chloride Concentration On Loading.

Cd; W_R/V = 0.046g/ml.

Resin wt (g)	Cal. dry wt. (g)	Initial pH	Final pH	Wt.loaded metal(mg)	Loading %
9.20	4.64	0.28	1.24	<1	<0.01
9.24	4.66	0.50	3.56	1.5	0.03
9.14	4.61	0.68	4.28	2	0.05
9.31	4.69	0.97	4.74	3	0.07
9.37	4.72	1.28	4.96	3	0.07
9.09	4.58	3.14	6.5	2	0.05

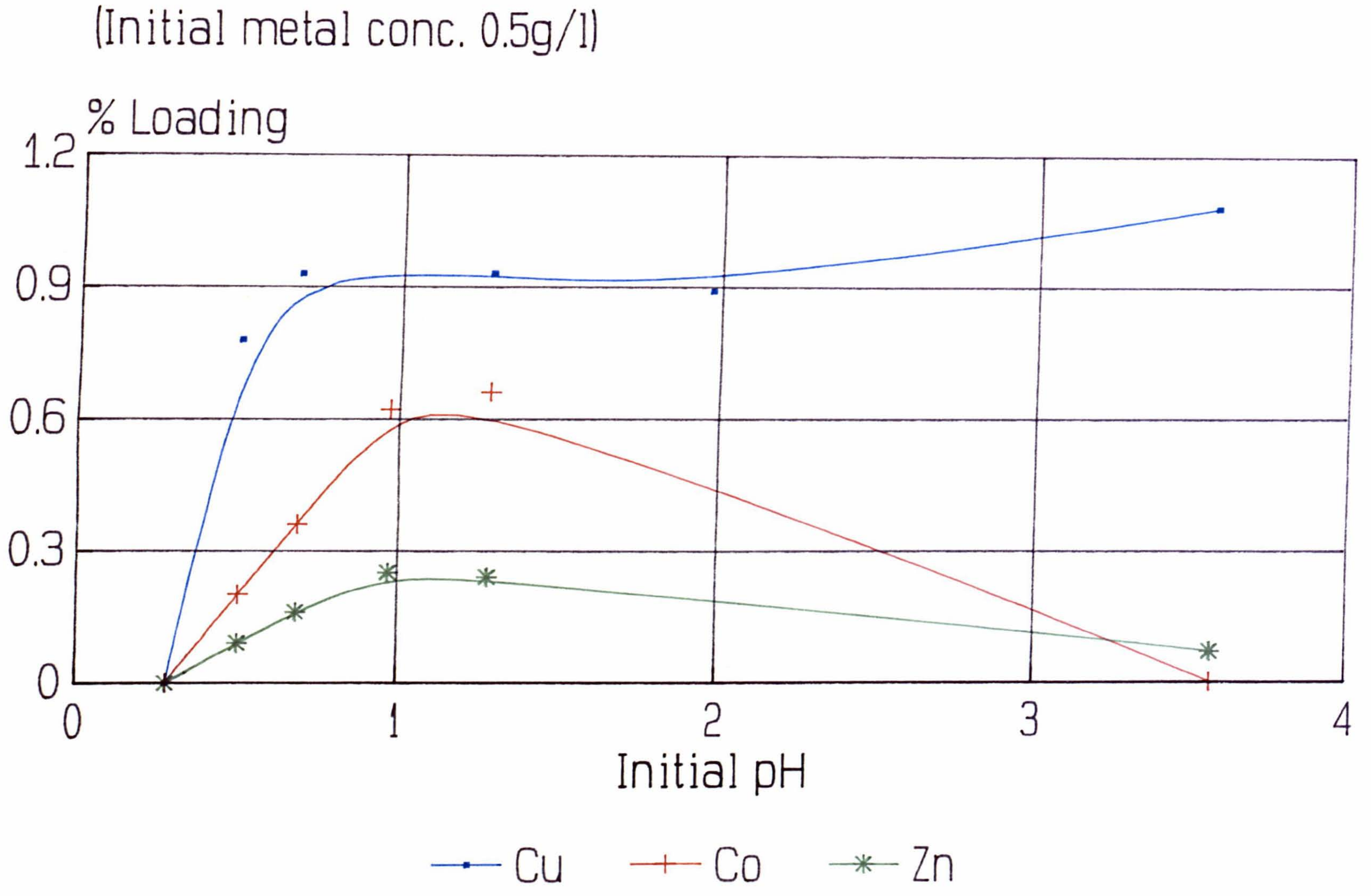


Figure 4.4
Effect Of High Chloride Conc. On Loading

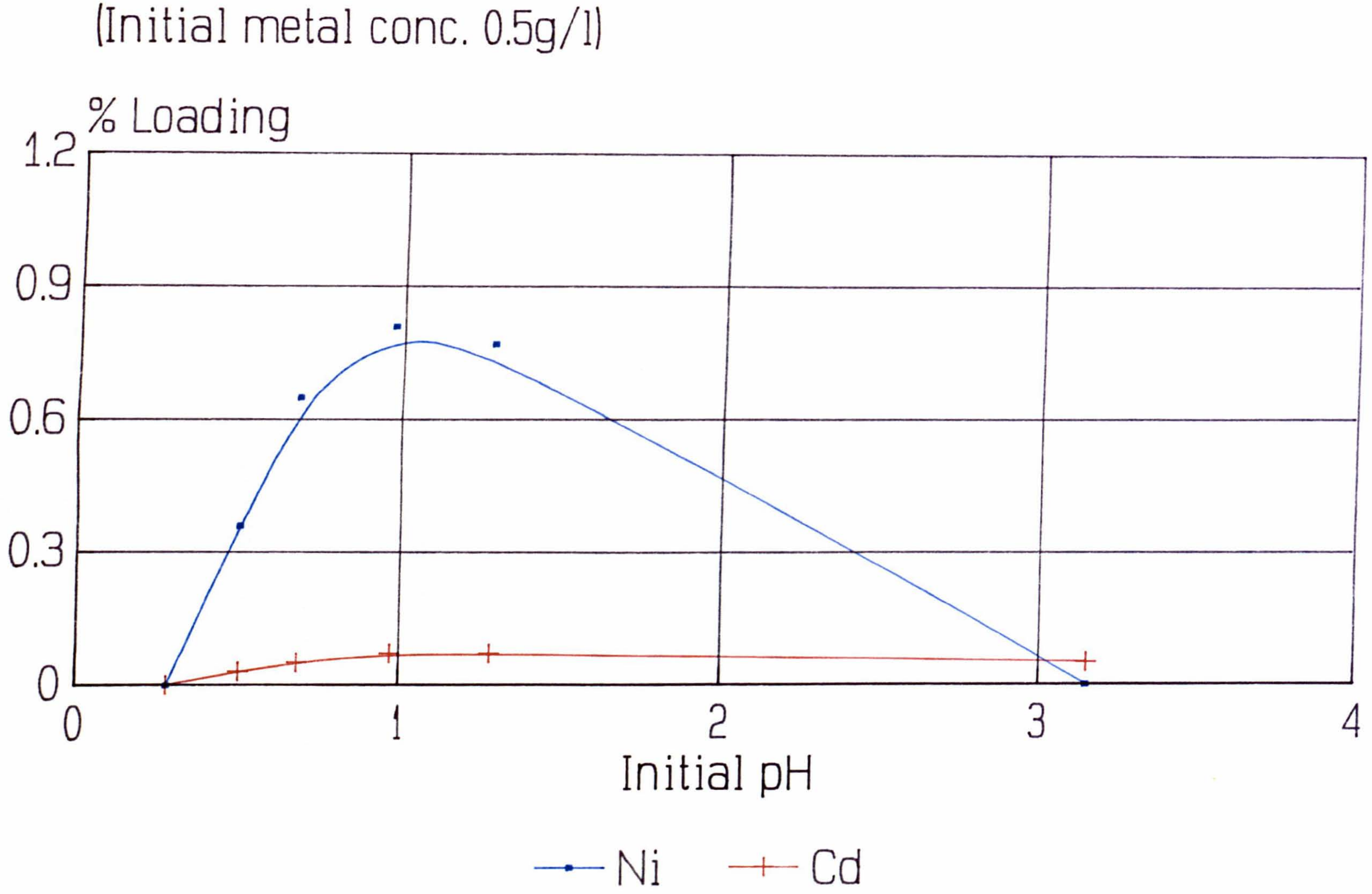


Figure 4.5
Effect Of High Chloride Conc. On Loading

4.5.7 Solution purification.

The application of PVP to the purification of metal chloride solutions, was investigated in terms of the effect in variations of both solution pH and the W_R/V value on the concentration of the residual metal impurity. The results of such investigations, involving Alkali Metal chloride solutions, were then used to choose favourable conditions for the purification of various concentrated Transition Metal chloride solutions.

4.5.7a Effect of pH.

The ability of the resin to reduce concentration levels of different metal impurities, in concentrated KCl solutions of varying initial pH, was investigated by determining the metal impurity concentration after the equilibration of a quantity of activated resin in the sample solution.

Residual metal impurity concentrations were determined using the procedure described in 4.5.2, for solutions containing 40g/l KCl, and initially 500ppm Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+}, and varying in initial pH from 0.28 to approximately 4. Solutions containing no KCl were also investigated.

Results are given in Table 4.11 and displayed graphically in Figures 4.6 and 4.7, from which it can be seen that maximum solution purification occurs within the pH range 0.8 to 1.1, (as would have been predicted using the data obtained from the previous experiments), with almost quantitative removal within this region for Cu^{2+}, Zn^{2+} and Cd^{2+} in concentrated KCl solutions, and for Cu^{2+} and Cd^{2+} in dilute solutions. In all cases, a high chloride concentration improves solution purification.

4.5.7b Effect of increasing the W_R/V value.

Results of the previous experiment show that maximum solution purification occurs in solutions with an initial pH within the range 0.8 to 1.1. The effect of increasing the W_R/V value was investigated with a view to achieving quantitative removal of Cu^{2+}, Cd^{2+} and Zn^{2+} from a 40g/l KCl solution.

Residual concentrations were investigated following the general procedure described in 4.5.2 and with solutions containing initially 500ppm Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} at pH 1.0. The solutions were equilibrated with different weights of activated resin, to give a W_R/V value varying from 0.05 to 0.30g/ml. Similar solutions containing no KCl were also investigated.

The results are given in table 4.12, and show that concentrations of the metals under study are reduced to <2ppm in the KCl solutions, except for Co^{2+}, which was reduced to a minimum of not less than 100ppm.

4.5.7c Purification of transition metal chloride solutions.

Separate solutions of 40g/l $NiCl_2$ and $CoCl_2$, at pH 3.40 and 3.55

respectively, both containing a 0.5g/l impurity of Cu^{2+}; and a 40g/l solution of $CuCl_2$ at pH 0.28, containing 0.5g/l impurities of Zn^{2+} and Cd^{2+}, were treated with a quantity of resin to give a W_R/V value equal to 0.048g/ml. Residual metal impurity concentrations were determined in the usual way.

Results are given in table 4.13, and show that Cu^{2+} can be reduced to <100ppm in both concentrated $NiCl_2$ and $CoCl_2$ solutions, and that levels of Zn^{2+} and Cd^{2+} in the concentrated $CuCl_2$ solution, can be reduced to <180ppm and <55ppm respectively, with, in all cases, negligible extraction of the major metal ion present in solution.

Table 4.11 Solution Purification - Effect Of pH.

In 40g/l KCl solution (upper table)

In dilute solution (lower table)

Initial metal conc. 500ppm

W_R/V (g/ml)	Initial pH	Final pH	Residual metal concentration (ppm)				
			Cu	Ni	Co	Zn	Cd
0.050	0.28	1.24	500	491	518	183	60
0.049	0.50	3.46	8	310	470	69	45
0.049	0.68	4.07	2	109	354	9	14
0.048	0.97	4.39	2	95	303	6	5
0.050	1.37	4.84	6	268	419	15	10
0.050	3.18	5.25	99	449	479	394	375

0.049	0.28	1.15	528	520	560	432	114
0.046	0.50	2.58	218	508	557	429	183
0.047	0.68	3.24	44	420	521	295	64
0.049	0.97	3.70	31	329	463	220	22
0.047	1.37	4.10	74	334	458	253	27
0.047	2.94	4.83	237	452	479	411	284

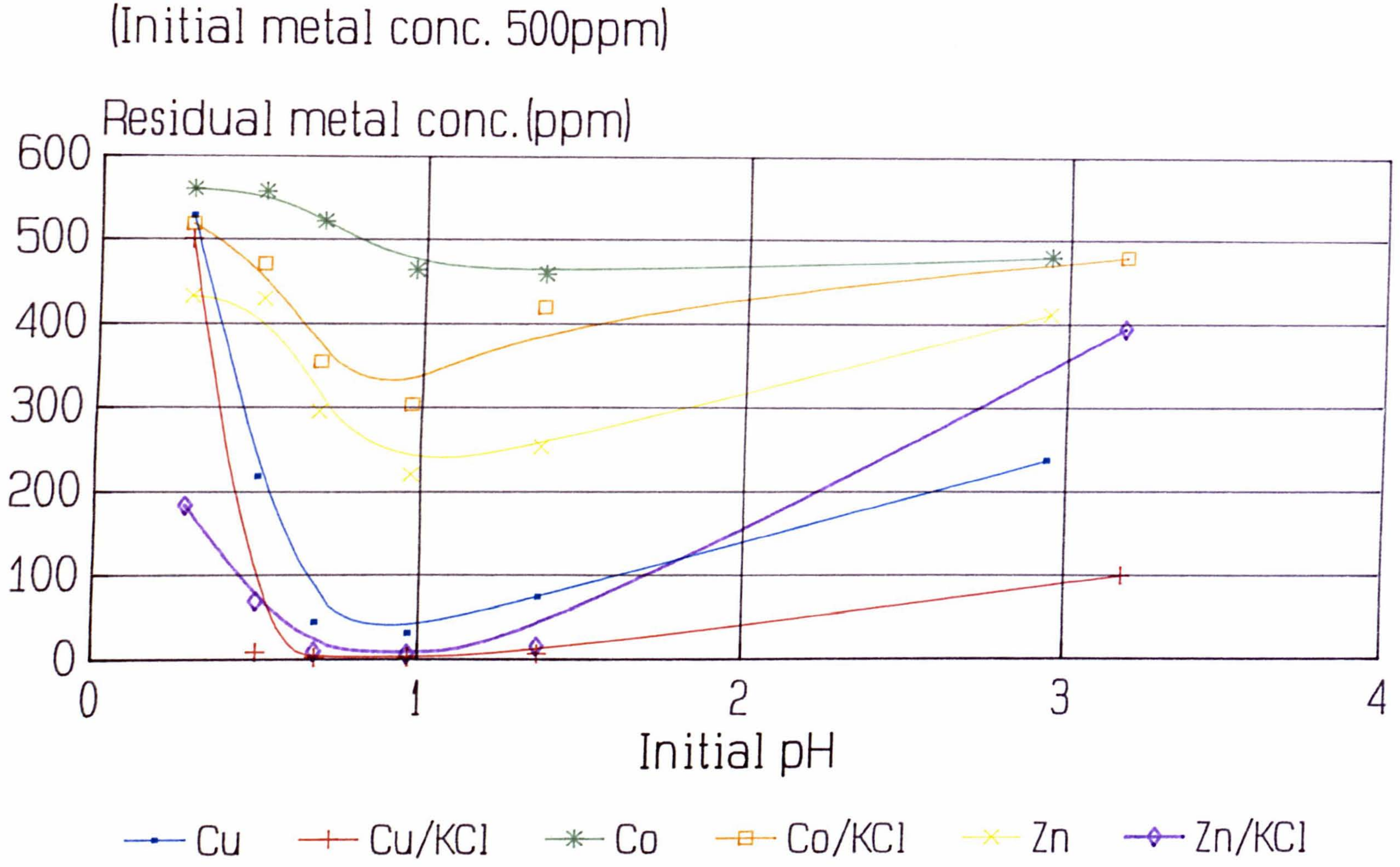


Figure 4.6
Effect Of pH On Purification Of 40g/l
KCl And Dilute Solutions

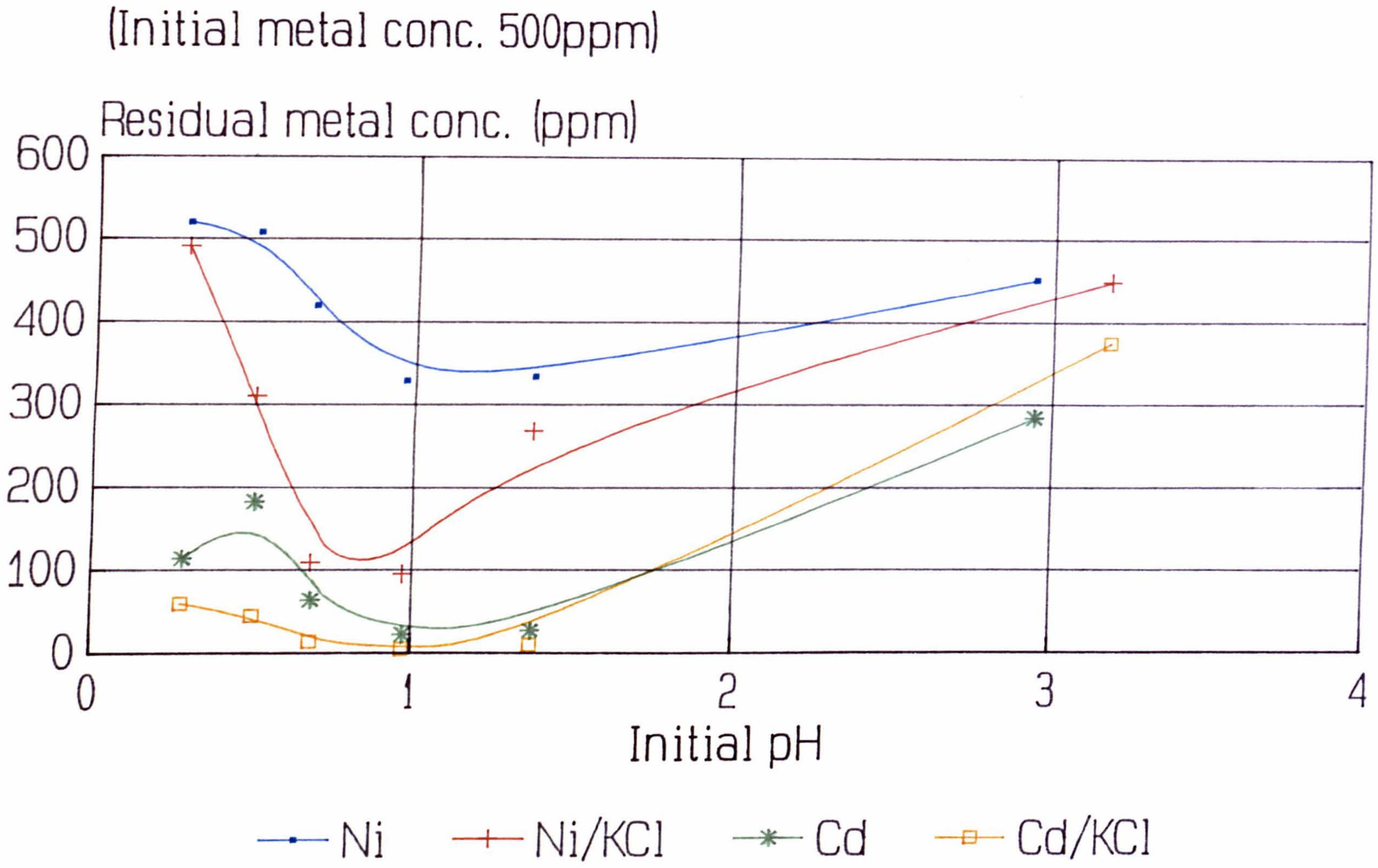


Figure 4.7
Effect Of pH On Purification Of 40g/l
KCl And Dilute Solutions

Table 4.12 Solution Purification - Effect Of W_R/V.

In 40g/l KCl solution (upper table)

In dilute solution (lower table)

W_R/V	Final	Residual metal concentration (ppm)				
(g/ml)	pH	Cu	Ni	Co	Zn	Cd
0.051	4.58	2	77	274	4	4
0.104	4.92	<1	23	149	2	2
0.204	5.31	<1	21	135	2	<2
0.296	5.60	<1	16	112	<2	<2

W_R/V	Final	Residual metal concentration (ppm)				
(g/ml)	pH	Cu	Ni	Co	Zn	Cd
0.051	3.72	30	321	458	225	19
0.103	4.51	11	148	289	109	9
0.205	4.92	7	132	272	84	5
0.295	5.52	4	125	258	59	3

Table 4.13 Solution Purification - Transition Metal Chloride Soln.

Soln	W_R/V	Initial	Final	Residual metal conc.(ppm)			Metal removed %		
	(g/ml)	pH	pH	Zn	Cd	Cu	Ni	Co	Cu
$CuCl_2$	0.049	0.28	1.23	171	51	--	--	--	0.11
$NiCl_2$	0.045	3.40	4.98	--	--	93	0.04	--	--
$CoCl_2$	0.046	3.48	5.04	--	--	89	--	0.04	--

4.5.8 Summary and conclusions.

The results of the experimental work have shown that the weakly basic resin, poly-4-vinyl pyridine, prepared in the free base form, is able to extract metals from chloride solutions, with an efficiency which depends on the pH and composition of the solution. For maximum metal extraction, the optimum initial pH of the solution was found to be within the range 0.8 to 1.2 for a W_R/V ratio of 0.045 to 0.050g/ml.

Increasing the metal chloride concentration in solution was found to increase the extractive power of the resin, relative to that metal. A similar effect was found to occur with all resin active metals generally when experiments were carried out in solutions containing a high concentration of KCl.

The resin exhibited a metal preference, the order of which depended strongly upon experimental conditions. Loading experiments indicated a selectivity decreasing in the order $Cu^{2+} \gg Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$ and $Cu^{2+} > Ni^{2+} > Co^{2+} \gg Zn^{2+} \gg Cd^{2+}$ for solutions which are dilute, and containing 40g/l KCl, respectively, with no retention shown for Alkali and Alkaline Earth metals. However, the solution purification experiments showed a selectivity decreasing in the order $Cu^{2+} = Cd^{2+} \gg Zn^{2+} > Ni^{2+} \gg Co^{2+}$ and $Cu^{2+} = Cd^{2+} = Zn^{2+} > Ni^{2+} \gg Co^{2+}$ for dilute and 40g/l KCl solutions respectively.

On comparison of the sequences indicated by the two experimental approaches, it can be seen that the order of preference is considerably different. This can be explained by making the assumption that both strong and weak interactions are involved in metal retention by the resin. The strong interactions being composed of strong electrostatic forces, (anion exchange), and coordinate bonding, and the weak interactions comprising weak electrostatic forces and sorption. In the case of the solution purification approach, the resin, after equilibration with the metal containing solution, is not subjected to further treatment by way of washing or filtration. Weak interactions between metal species and resin therefore remained intact. However, in the loading experiments, isolation of the resin, followed by washing and suction filtration, it may be assumed that only strong interactions remain intact, reducing the apparent metal loading of the resin relative to the loading values infered by the solution purification experiments.

Assuming the involvement of the strong and weak interactions, it can be said that Cu^{2+}, Co^{2+} and Ni^{2+} show predominantly strong interactions with the resin, whereas Cd^{2+} is retained by weak interactions, and Zn^{2+} interactions of both types.

It cannot be overstressed, that the differences observed in the apparent metal selectivities, when comparing data from both experimental approaches, is of great significance in the practical application of the resin, whether in a small scale or industrial enviroment.

Whether or not the resin can be described as possessing anion exchange behaviour, with metal species in solution, is open to question. The selectivity sequences infered by the experimental data, (particularly those data obtained in solutions having high chloride concentrations, where the formation of anionic metal chloride complexes would be favourable), do tend to confirm the conclusions made by Kopylova that poly vinyl pyridines in general, interact with metals, predominantly by direct coordination of the metal to the pyridine nitrogen, (see 4.4), and certainly contradict the expected sequence based solely on the activity of the metals in complex halide formation [42]. (Approximately $Cu^{2+}=Cd^{2+}=Zn^{2+}>Co^{2+}>>Ni^{2+}$). The inactivity of Ni^{2+} in such complex formation is well known.

An interesting property of the resin, is its apparent total inactivity toward Fe^{3+}. No retention of the metal by the resin was observed over the pH range investigated. Unfortunately, complications were encountered in solutions containing Fe^{3+}, because the final pH of the equilibrated solution was often above the value at which hydrolysis, and subsequent precipitation of the ion, occurs. Precipitation was found to occur in solutions of high ionic strength, whereas in dilute solutions, no precipitation occured because of the formation of colloidal ferric hydroxide.

With the data obtained from the experimental work, predictions can be made on the behaviour of the resin in column chromotography. For instance, metal separations involving Ni^{2+} and Co^{2+}; Cu^{2+} and Zn^{2+}; Cd^{2+} and Ni^{2+}; and Cu^{2+} and Co^{2+} should be possible, with excellent separation expected for the latter two cases. Quantitative removal from solution of Cu^{2+}, Cd^{2+} and Zn^{2+}, with a column technique, should easily be attained.

In conclusion, it can be said that poly-4-vinyl pyridine has shown good metal retentive properties in a variety of solutions. The data attained will allow predictions to be made on the performance of the resin in future metal recovery and solution purification operations. Predictions would be particularly accurate in applications involving solutions and conditions similar to those investigated in the experimental work in this chapter.

4.6 References.

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APPENDIX 1

APPLICATION OF ATOMIC ABSORPTION SPECTROSCOPY.

Atomic absorption spectroscopy, (A.A.S.), was used extensively throughout the practical work described in the thesis, for the determination of metal concentrations in solution. Analyses were performed on a Perkin Elmer spectrometer, with a choice of air/acetylene or air/nitrous oxide flame atomisation. Measurement of absorption was by digital readout.

A.A.S. was applied particularly to the determination of impurity metals in process solutions, and principally to the solution analysis of Cu, Fe, Pb, and Mn in $ZnCl_2$, Fe, Zn, Pb, Mn, and Al in $CuCl_2$, and of Cu, Fe, Zn, Co and Al in $NiCl_2$.

Because of the importance of the technique to the validity of the results given in the thesis, emphasis was placed on ensuring the accuracy of the analyses by:

a) The use of accurate calibration standards.

b) Frequent calibration during analysis, and thorough checking of the sample readings.

c) Determining the linear concentration/absorption range, and working, as far as possible, within this range.

d) Being aware of, and counteracting, interferences.

Because of the complexity of many of the solutions under investigation, e.g. leachates, d) was considered of great importance. To neutralise the effects of interferences arising from such solutions, the method of standard additions was applied extensively, particularly to solutions containing very high concentrations of primary metal relative to the impurity metal of interest, an example of which is the analysis of impurities in concentrated $ZnCl_2$ solutions, (chapter 3). In this example, the most prevalent interference was found to arise from the high salt concentration, which imparted a relatively high viscosity to the analyte solution, even after necessary dilution, resulting in a lower rate of aspiration and therefore an erroneously low absorption figure. This type of interference was investigated early in the practical work, some examples of the effect are illustrated in figures A1.1 and A1.2.

A.A.S. was found to be a reliable and effective analytical technique when applied to the practical work within the thesis.

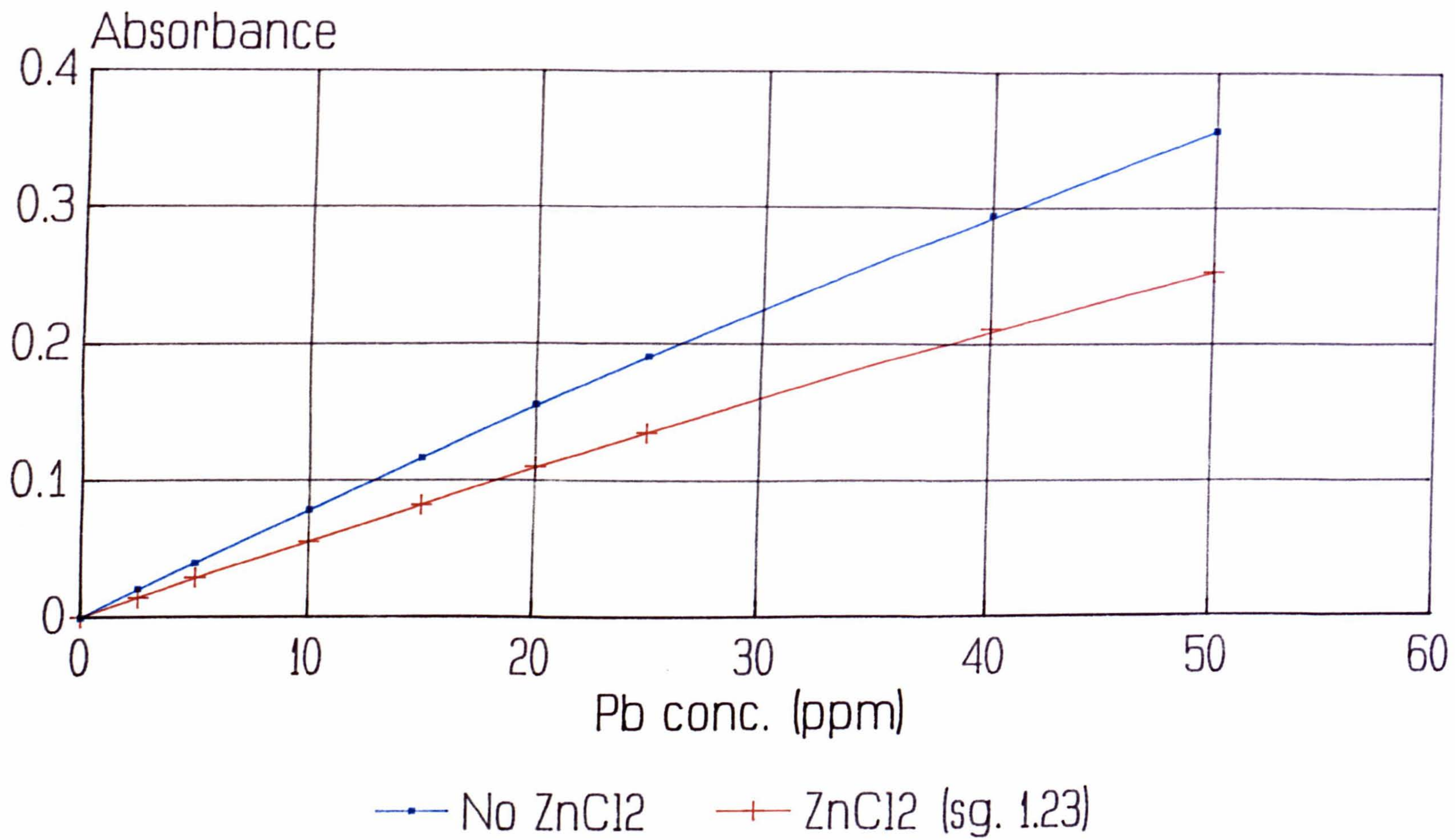

Figure A1.1
A.A.S. Interference Of High ZnCl2 Conc.
On Pb In Aqueous Solution

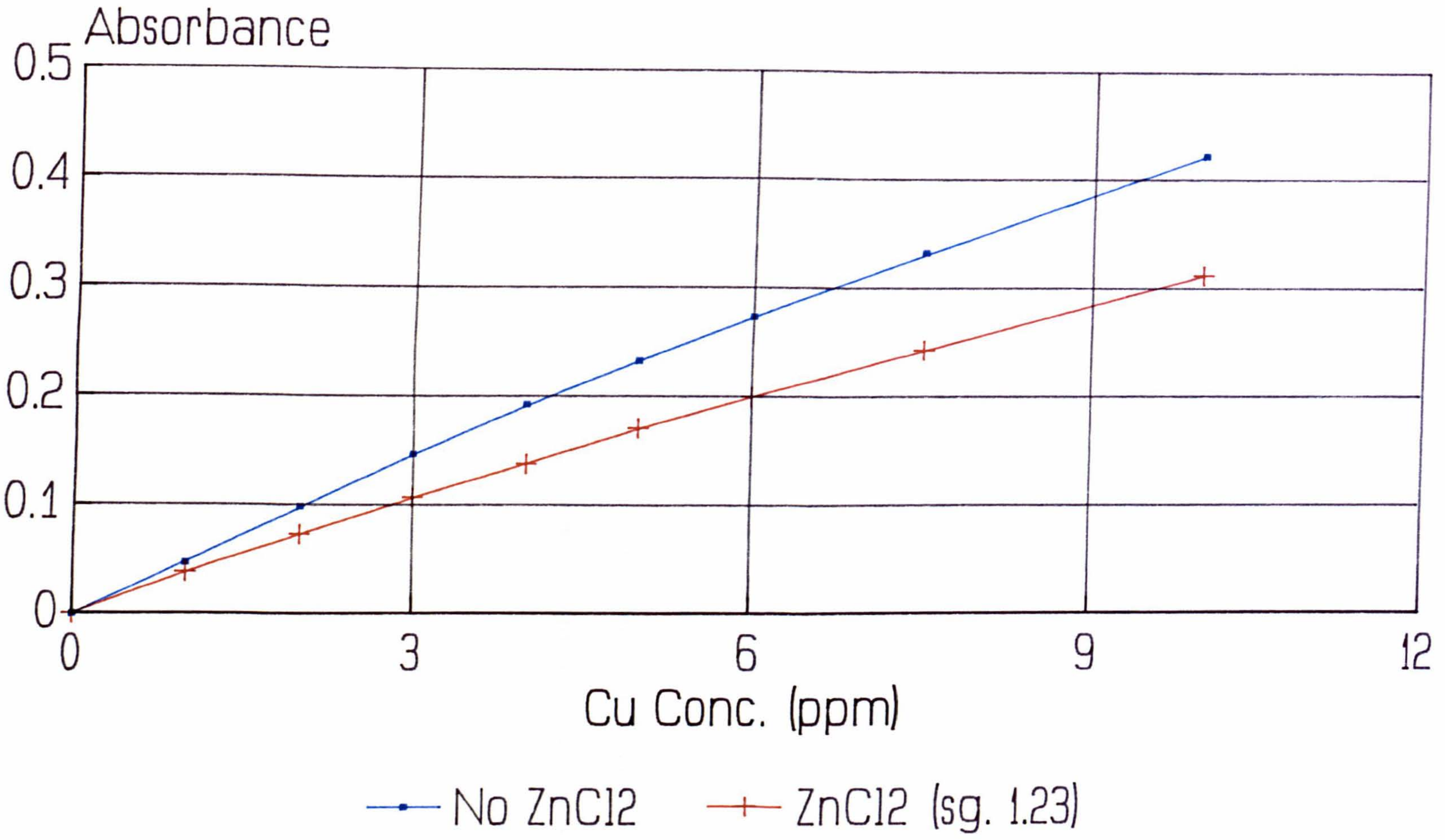

Figure A1.2
A.A.S. Interference Of High ZnCl2 Conc.
On Cu In Aqueous Solution

APPENDIX 2

SAMPLE ANALYSIS BY E.D.A.X.

E.D.A.X. (Energy Dispersive Analysis of Xrays) was used, where required, to give semi-quantitative data on the elemental composition of solid samples, particularly to raw materials containing the metal value, and leach residues, to give data on the impurity metals, and leach selectivity, respectively.

Sample excitation was by a J.E.O.L. JEM 100B transmission electron microprobe, (40KV beam), with a scanning attachment. Xray fluorescence was recorded by a computer based EDAX 9100/60 system, with results shown by VDU. The software incorporated a Z.A.F. program, to apply corrections to computations, to allow for atomic number, (Z), reabsorbtion of xrays, (A), and resultant refluorescence, (F). With this software, a more accurate semi-quantitative analysis was achieved.

APPENDIX 3

MEASUREMENT OF ALUMINIUM CONCENTRATION IN CONCENTRATED ZINC CHLORIDE SOLUTIONS.

Because of the relative insensitivity of Al analysis by AAS, a technique, with a more suitable sensitivity, was found and adapted to the measurement of aluminium concentrations in concentrated $ZnCl_2$ solutions [1].

The technique involved the measurement of absorbance with a Corning Absorptiometer, at approximately 550nm (605 filter), of a Al-Eriochrome Cyanine R dye complex. Initial measurements were performed in solutions at pH 6, but because of problems concerning the precipitation of zinc hydroxide at this pH, a modified method was used, involving determinations of absorbance, at pH 3, in alcoholic solutions [2,3]. Because of the relatively high concentrations of $ZnCl_2$ necessarily present in the sample solution, the effect of this compound on the Al-dye absorbance was investigated before serious use of the analysis technique was considered. Results showed that over the greater part of the Al concentration range investigated, a reduction in measured absorbance occured when $ZnCl_2$ was present, and that the magnitude of the reduction varied with concentration of the salt. Figure A3.1 illustrates the effect. Whilst this interference posed no great problems, calibration standards were prepared to match, as accurately as possible, the concentration of $ZnCl_2$ in the sample solution.

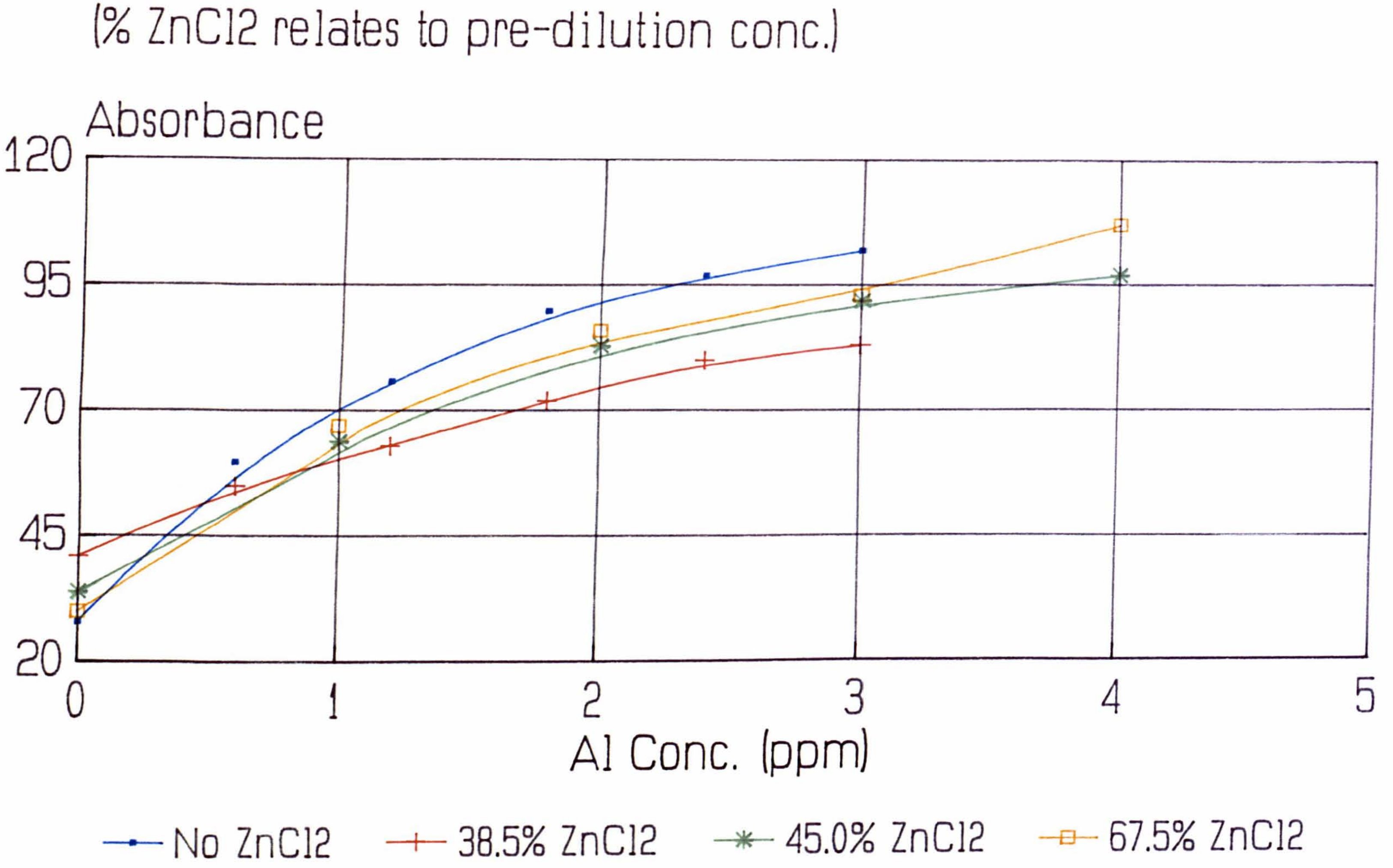

Figure A3.1
Effect Of ZnCl2 Conc. On
Al-Dye Absorbance

The method used was as follows:

Standards.

1) 1 to 10ml, depending on sample concentration, of a solution of $ZnCl_2$ in hydrochloric acid, was adjusted to pH3 with ammonia and 25ml of pH3 acetic acid/ammonium acetate buffer added.

2) 0 to 5ml of 100ugAl/ml aluminium chloride solution was added, followed by 50ml of A.R.grade ethanol and 2ml of 0.2% dye in water.

3) The solution was made up to 100ml, and left for 20 minutes for the colour to develop fully.

Sample.

1) An aliquot of sample solution was substituted for the $ZnCl_2$ solution, and then treated as above but ommiting the Al standard addition.

New dye solution was prepared daily, and measurements were performed within 1 hour of standard and sample preparation. Good reproducibility was observed.

References.

1) Vogel. "Textbook of Quantitative Analysis". page 729.
2) Vogel. "Textbook of Quantitative Analysis". page 611.
3) C. R. Acad. Bulg. Sci. 29 1313-1316 (1976).